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THE
ELECTROLYTIC DISSOCIATION THEORY
WITH SOME OF ITS APPLICATIONS

AN ELEMENTARY TREATISE
FOR THE USE OF
STUDENTS OF CHEMISTRY

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PREFACE

In this little treatise the authors have sought to bring together, in small compass, material relating to the Electrolytic Dissociation Theory which is now somewhat widely distributed throughout many of our excellent textbooks. The method of presentation is that which they have found serviceable in enabling their students to comprehend the main facts which are today generally accepted as supporting the Theory, and to understand its application to important types of chemical change.

While the book has been written primarily for the use of students, the authors have also kept in mind its probable usefulness to the teacher in preparatory school or college, who may desire to gain in a short time an acquaintance with the fundamental facts and principles in this interesting field. In this connection, however, they desire to express their firm conviction that this Theory should be touched upon in only the most elementary way in the secondary schools; but this does not, of course, make it less necessary that the well-informed teacher should be prepared to meet the inquiries of the occasional unusually mature and thoughtful pupil.

More has been included in this manual than the authors have found it advisable for the college student who is just beginning the study of chemical science to attempt to master, and quite as much as many students who have already had a year of chemical experience in a preparatory school will be able to thoroughly understand. Our experience has shown, however, that it is easier to maintain the interest of the thoughtful pupil if answers to some of the questions suggested to him by the discussions in the main body of the text are placed at his hand, when it is possible to do this without going too far afield. Most of the material of this nature has been printed in smaller type, and may be omitted without loss of continuity; and it is believed that in the course of a year of study the college student (even the beginner in chemistry, if he has some knowledge of physics) can be brought to understand the essential principles included in the main text. To insure this it is necessary that the instructor should lose no opportunity throughout his course to emphasize the application of a principle, after it has once been introduced.

The attempt to present the subject-matter in a simple form, and at the same time to avoid inaccurate statements, has sometimes led to a conflict of ideals, as, for example, in the application of the Law of Mass Action to strong electrolytes. Nothing is said in this connection of the unexplained fact that such electrolytes apparently do not rigidly obey this law, since to discuss this topic would seriously complicate an important statement without corresponding advantage. We believe, however, that in such cases no violence has been done to the principles of physical chemistry, and that no impressions have been given which it will be difficult for the student to unlearn if he pursues the subject to its more advanced stages.

The application of the ionic theory to indicators has been omitted altogether, as the present state of our knowledge seems to indicate that complicated rearrangements of the atoms within the molecules of organic substances are involved, with which it would be beyond the scope of this treatise to deal.

The authors desire to acknowledge their indebtedness to many of the standard text-books, and especially to Smith's "Laboratory Outline of General Chemistry" for suggestions as to laboratory experiments. They would also acknowledge the valuable assistance rendered by Dr. Miles S. Sherrill, and the friendly and helpful criticisms of other members of the instructing staff of the Massachusetts Institute of Technology.

H. P. TALBOT.
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September, 1905.

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CHAPTER I

EVIDENCES OF ELECTROLYTIC DISSOCIATION AFFORDED BY A STUDY OF THE PROPERTIES OF SOLUTIONS

1. If the various forms of matter are studied with reference to their ability to transmit an electric current, it is found that some, such as glass, hard rubber, or alcohol, do not allow an appreciable amount of electricity to pass through them, while others permit the passage of electricity with comparative readiness. The former are called *non-conductors;* the latter, *conductors.* The conductors, in turn, may be subdivided into two classes with reference to the manner in which they transmit the current, namely, *metallic conductors* and *electrolytic conductors.* Platinum or copper wires, or the carbon filaments of incandescent lamps, are of the first variety, and conduct the current without undergoing any permanent alterations, while in conductors of the second variety (comprising salts when in the molten condition, or solutions, particularly aqueous solutions, of acids, bases, or salts) the passage of the current is accompanied by a separation of the components of the conductor. This electrolytic conduction can only take place in fluid bodies the components of which gradually collect at the poles, that is, at the points where the current enters and leaves the fluid. Bodies which conduct in this manner are known as *electrolytes*, and the process of conduction accompanied by the separation of the constituents of the electrolyte is called *electrolysis.*

It was to explain electrolysis, together with certain other peculiar properties possessed only by those solutions which conduct electricity, that in 1887 Arrhenius, a Swedish physicist, was led to propose the Theory of Electrolytic Dissociation.

This theory assumes that a certain proportion of the dissolved molecules of electrolytes are dissociated into simpler component parts, called *ions*, and that each of these ions has an effect upon many of the properties of solutions equal to that of a whole molecule. It is the purpose of the following pages to present some of the important considerations which have led to the general acceptance of this theory, and to illustrate the applications of the theory to certain typical chemical changes.

With a very few exceptions all solid non-metallic substances, as well as all pure liquids and gases, are non-conductors of electricity at ordinary temperatures. Thus a crystal of sodium chloride is a non-conductor, and pure water is a non-conductor. If, however, the crystallized sodium chloride is heated until it fuses, or, still more easily, if it is dissolved in water, the result is an excellent conductor of electricity. The discussion which follows will be confined mainly to the latter case, namely, that in which a non-conductor, upon being dissolved in a non-conducting liquid at ordinary temperatures, becomes a good conductor of electricity.

It must first be noted that not all solutions exhibit this phenomenon of electrolytic conduction, and that those solutions which do possess this property also possess certain other remarkable properties which are absent in solutions which do not allow a current to pass through them. These properties may be summarized as follows: —

I. Such solutions freeze at an abnormally low temperature.
II. They boil at an abnormally high temperature.
III. The osmotic pressure of the dissolved substance is abnormally great.
IV. The dissolved substance exhibits great chemical activity.
V. They permit the passage of an electric current.

These five striking properties will first be considered, and it will not only be seen that if each is carefully examined it leads to the conclusion expressed by the Dissociation Theory, as outlined above, but it will be further shown that if the proportion of the molecules of an electrolyte which are dissociated is estimated from data based upon an independent study of each of the properties, the values obtained are substantially concordant.

THE LOWERING OF THE FREEZING POINT

2. When any substance is dissolved in a pure liquid the resulting solution freezes at a lower temperature than the solvent alone, and for any given substance the amount by which the freezing point is lowered below that of the pure solvent is in proportion to the quantity of the

substance dissolved; for example, the lowering of the freezing point by the solution of 20 grams of sugar in a specific volume of water (say 1,000 c.c.) is twice as great as that produced by the solution of 10 grams in the same volume. Moreover, if 60 grams of urea, 46 grams of ethyl alcohol, and 342 grams of sugar are each dissolved in 1,000 grams of water, the resulting solutions freeze at $-1.86°$ C. The quantities named are the molecular weights in grams respectively of the three substances, and these amounts will hereafter be designated as *mols*.

The mol (60 grams) of urea is, of course, made up of an exceedingly large number of the very minute individual molecules, and the same is true of the mol (342 grams) of sugar; yet, since the quantities expressed by the mols stand in the same relation to each other as the molecular weights of the two substances, the number of actual molecules must be the same in both cases. Solutions which contain, in a given volume, any other quantities of these substances which stand in the same proportion to each other as their molecular weights must also contain the same actual number of molecules; that is, be equi-molal.

The above statement holds true for all bodies which do not yield solutions which conduct an electric current. Such bodies are termed *non-electrolytes,* in distinction from those bodies which in solution do conduct a current, and are termed electrolytes. Thus, the freezing point of a solution of any non-electrolyte containing 1 mol in 1,000 grams of water is 1.86° C. lower than the freezing point of the water. This quantity is known as the *molecular lowering of the freezing point*, and it is easy to see that if this molecular lowering for water has once been established from experiments with a considerable number of substances of known molecular weight, then the number of mols of any non-electrolyte dissolved in water may be found by determining the freezing point of its solution.

For example, a solution of 50 grams of wood alcohol in 1,000 grams of water is found to freeze at $-2.90°$. Since every mol of a non-electrolyte should cause a lowering of the freezing point of 1.86°, the number of mols in the solution must be $\frac{2.90}{1.86}$, or 1.56. This is in accordance with the facts, because the amount dissolved (50 grams) must represent $\frac{50}{32}$, or 1.56 mols, since the mol of wood alcohol (CH_3OH) is 32 grams.

If the lowering of the freezing point produced by a given number of mols of an electrolyte is compared with that produced by the same number of mols of a non-electrolyte (such as the wood alcohol of the preceding paragraph) it is found to be abnormally large. If, however, the principle stated above, that the number of mols of the dissolved substance may be measured by the extent of the lowering of the freezing point, holds true, then it must follow that a given number of molecules of an electrolyte (using the term molecule in its ordinary chemical sense), when in solution, are in reality broken up into a greater number of smaller molecules of some sort, each one of which has the same effect in depressing the freezing point of the solution as one of the original undecomposed molecules, or as a molecule of a non-electrolyte.

An example will make this clear. A solution containing 5.85 grams of sodium chloride to the liter is found by experiment to freeze at − 0.350° C. If sodium chloride were a non-electrolyte, that is, if it formed only NaCl-molecules in a solution, the freezing point would be − 0.186°, because, since this solution contains 5.85 grams of dissolved substance in 1,000 grams of solvent, and the molecular weight of NaCl is 58.5, the 5.85 grams should constitute 0.100 mol, and should depress the freezing point to the extent of $\frac{5.85}{58.5} \times 1.86$, or 0.186°. That the actual lowering is 0.350°, or $\frac{.350}{.186} = 1.88$ times greater than that which should result if the sodium chloride behaved in the same manner as the non-electrolytes illustrated above, shows that the solution contains a larger number of molecules than the number of chemical molecules (NaCl). It is easily seen that this would be explained if, for example, out of 1,000 of the original NaCl-molecules 880 should, when dissolved, dissociate into the smaller individuals Na and Cl, while 120 remained in the form of the larger NaCl aggregates. The total number of molecules would then be 1,880, which is 1.88 times the number of the chemical molecules (NaCl.) Likewise, of 1,000 molecules of such a body as calcium chloride, $CaCl_2$, 750 molecules might dissociate into 750 of the smaller individuals Ca and 1,500 of Cl, while there remained 250 of the $CaCl_2$ aggregates, thus giving 2,500 molecules in solution. This supposition is in accord with the actual freezing point of a calcium chloride solution, which indicates 2.5 times as many molecules as the number of chemical molecules ($CaCl_2$).

It may at once be asked whether such a supposition as is here suggested is justifiable, since a solution of sodium chloride exhibits none of the well-known properties of sodium or chlorine. The full explanation of the difference between these smaller molecules (part-molecules) and ordinary atoms of elements in the uncombined state can best be given in a later paragraph (see page 12), but it may be briefly stated here that it is due to the electrical charges which reside upon these part-molecules, essentially altering their behavior. In such bodies as ammonium nitrate, the breaking down of the chemical molecules is not into single atoms, but into groups of atoms, as NH_4 and NO_3, which also bear electrical charges.

THE RAISING OF THE BOILING POINT

3. If any non-volatile substance is dissolved in any liquid, the temperature at which that liquid boils is raised. The same principles are found to hold with respect to the raising of the boiling point which have just been outlined for the lowering of the freezing point. This property of solutions may, therefore, likewise be made use of to determine the number of molecules of the dissolved substance which a solution contains.

The molecular raising of the boiling point of water is 0.52° ; that is, if 1 liter of an aqueous solution contains 1 mol of any non-electrolyte which does not itself boil at a low temperature, the solution boils 0.52° C. higher than pure water. All solutions of electrolytes boil at abnormally high temperatures just as they freeze at abnormally low temperatures, and the extent to which each electrolyte is dissociated into smaller molecules is shown to be the same by means of this method as by the method previously discussed. For example, a 3.3 per cent. solution of sodium chloride boils at 100.50° C. If it were an undissociated body the boiling point would be raised only to the extent of $\frac{33}{58.5} \times 0.52$, or 0.30°. That the actual raising is $\frac{0.50}{0.30}$, or 1 7 times this amount, leads to the same conclusion as before, namely, that in solution about 0.7 of the NaCl aggregates are dissociated into smaller molecules. (The difference between this value and that deduced from the freezing point lowering [0.88] is not greater than would result from differing conditions and experimental difficulties.)

OSMOTIC PRESSURE

4. An understanding of the nature of the phenomenon known as osmotic pressure can best be gained through a consideration of gas pressure, which it closely resembles.

The molecules of a gas, as indeed of any substance not at the absolute zero of temperature, are in a state of rapid vibration, and, in their movement to and fro, the distance which a molecule may move in a straight line is limited to the space through which it may travel without colliding with another molecule, or with the walls of the containing vessel. When any two molecules of a gas collide they at once rebound with such force that each immediately escapes beyond the other's sphere of attraction, while the impacts of the molecules upon the walls of the containing vessel, against which they strike and then rebound, give rise to the phenomenon of gas pressure.

If the volume of a given quantity of gas is increased without changing the temperature, its pressure is diminished. This must follow if the statement of the nature of gas pressure is correct, because by increasing the volume the number of impacts which can be made by the molecules of the gas on a given area of containing wall is decreased. This is in accordance with Boyle's Law, which states that for a given quantity of gas kept at a constant temperature the pressure is inversely proportional to the volume, or that

$$\textit{pressure} \times \textit{volume} = \textit{constant}.$$

If the temperature of a gas is increased without allowing its volume to change, its pressure is increased. This follows from the fact that temperature is the measure of the intensity of the vibratory motion of the molecules of a substance. If the molecules of a gas vibrate faster, they must necessarily strike oftener and harder upon the walls of the containing vessel, or, in other words, they must exert a greater pressure. This accords with the Law of Charles, which states that the pressure of a gas, kept at a constant volume, is proportional to the absolute temperature.

If two vessels of the same size contain the same number of molecules of different gases at the same temperature, each gas exerts the same pressure. This is the converse of Avogadro's Theory, which states that two equal volumes of gas at the same temperature and pressure contain the same number of molecules. From this it appears that the pressure exerted by a body of gas at a given temperature and volume depends solely upon the number, and in no way upon the kind, of its molecules. In other words, the rapidity of vibration of the molecules of hydrogen at any given temperature so far exceeds that of the molecules of oxygen that a given number of the molecules of the former element exerts the same pressure as the same number of molecules of the latter element. The pressures of two equal volumes of gases at the same temperature stand, therefore, in the same relations as the numbers of molecules of the gases in these volumes.

A molecular weight in grams (mol) of *any* gas, as 17 grams of ammonia gas (NH_3) or 2 grams of hydrogen, at the standard pressure, 760 mm. of mercury, and at the standard temperature, 0° C., occupies a volume equal to 22.4 liters; if it is compressed to 1 liter, it will exert a pressure equal to 22.4 atmospheres, *i. e.*, 22.4×760 mm.

5. When a substance is dissolved its molecules vibrate to and fro in the solvent in the same manner as do the molecules of a gas in the space which the gas occupies. These molecules of dissolved substance will, therefore, exert a pressure against an opposing surface in exactly the same manner as the molecules of a gas. This is known as *osmotic pressure*. If by any means it were possible to measure this osmotic pressure of the dissolved molecules separately from the pressure of the solvent, it is evident from what has been said concerning gas pressure that such measurements might furnish another means of determining the number of molecules of the substance in solution. To illustrate how such measurements might be possible, let us imagine a fish seine with which fishermen have succeeded in encircling a school of mackerel. Water passes freely through the net and exerts no pressure, but the fish are too large to pass through the meshes. In their

efforts to escape they strike against the net and thus exert a pressure upon it. Similarly, if a mesh can be prepared so fine that molecules of a substance dissolved in water cannot pass through it, but still so large that water molecules may readily pass, it would furnish a means of measuring osmotic pressure. Such meshes do exist, and are called osmotic membranes. The walls of plant cells, many animal membranes, and many artificially prepared films are of this semi-permeable character.

6. The formation of such membranes, as well as the existence of osmotic pressure, may be qualitatively shown by what may be called the *mineral flower garden*, prepared as follows: small lumps or crystals of certain very soluble salts, *e.g.*, ferric chloride, copper chloride, nickel nitrate, cobalt chloride, or manganese sulphate, are dropped into a solution of sodium silicate (water glass, sp. gr. 1.1). Their behavior resembles that of growing seeds, as they appear to immediately sprout and send up shoots toward the surface of the liquid, which grow with a visible rapidity. In fact, the salts have at once commenced to dissolve, forming thin layers of very concentrated solution about each lump. At the surface, separating each of these layers of solution from the water glass, there forms a film of the insoluble silicate of the metal. This film is an osmotic membrane which allows water to pass either in or out, but the molecules of salt, not being able to pass through, exert against it their osmotic pressure, and break it at its weakest part, which is always the top. This exposes a new surface of the salt solution to the sodium silicate, and a new film forms, which, in turn, is broken, thus permitting the growth of the little tube of the silicate of the metal. Clusters of these tubes of various colors give an appearance of plant growth within the liquid.

7. The quantitative measurement of osmotic pressure, although a matter of considerable difficulty, may still be made with a very fair degree of accuracy. A solution of 342 grams of sugar in 22.4 liters of water at 0° C. gives an osmotic pressure of 1 atmosphere, and the same osmotic pressure is shown by 1 mol of any other non-electrolyte in the same volume. The osmotic pressure being proportional to the concentration, if the above sugar solution is concentrated to a volume of 1 liter its osmotic pressure becomes 22.4 atmospheres. The osmotic pressure also increases with increasing temperature to the extent of $\frac{1}{273}$ of its amount at 0° C. for every 1° rise in temperature. It follows, therefore, that the Laws of Boyle and Charles apply to osmotic pressure as well as to gas pressure. Not only is this true, but it is further found that the *osmotic* pressure of a given amount of any non-electrolyte

is quantitatively the same as its *gas* pressure would be if it existed alone in the gaseous condition in the same volume as that occupied by its solution, and at the same temperature. This is seen to be true by comparing the figures given above (page 7) for the gas pressure of ammonia and the osmotic pressure of sugar. Avogadro's Theory applies, therefore, to solutions as well as to gases, and the osmotic pressure of a solution depends solely on the number of dissolved molecules, and in no wise upon their size or chemical nature.

Evidently, then, the measurement of the osmotic pressure of a solution may serve as a method of measuring the number of mols of dissolved substance present in exactly the same way as the measurement of gas pressure (or volume) may serve, by the aid of Avogadro's Theory, to determine the number of mols of a gas contained in a given volume.

It has already been noted that all solutions of electrolytes freeze at abnormally low and boil at abnormally high temperatures as compared with solutions of non-electrolytes. Similarly, it is found that the osmotic pressure produced by electrolytes is much in excess of that occasioned by corresponding amounts of non-electrolytes; and it is further found that if the number of mols in such solutions is calculated from the measurements of osmotic pressure, such substances as sodium chloride yield somewhat less than twice as many mols, while such as calcium chloride yield somewhat less than three times as many mols, as there are chemical mols according to the formulas NaCl and $CaCl_2$.

In very dilute solutions, where the chemical molecules are completely broken up into the part-molecules or ions, the osmotic pressure is, of course, twice and three times, respectively, that which would be expected if these electrolytes were not dissociated. In the case of solutions of such concentration as would more commonly come under consideration, and in which, due to their considerable concentration, it is impossible for all the molecules to be dissociated into ions, the measured osmotic pressure would indicate only about 1.8 and 2.5 times as many mols, respectively, as the number of chemical mols — figures which are in close accord with those obtained from the study of the lowering of the freezing point or the raising of the boiling point of such solutions.

8. This dissociation of the electrolyte is comparable with the behavior of ammonium chloride when it is vaporized. If the density of its vapor is measured, and the molecular weight is calculated from this value by the aid of Avogadro's Theory, it is found to be only one-half of that corresponding to the formula NH_4Cl. This fact is easily explained if each NH_4Cl-molecule is dissociated on heating into two smaller individuals, NH_3 and HCl. That this actually occurs may be shown by placing a lump of ammonium chloride in the middle of a glass tube between two plugs of asbestos wool, and heating the tube by means of a Bunsen flame. Of the two dissociation products ammonia is the lighter and diffuses more rapidly through the asbestos plugs, and if moistened bits of red and blue litmus paper are placed outside the asbestos the red will at first be turned blue at each end. This is due to absorption of ammonia by the moisture on the litmus paper with the formation of the alkaline ammonium hydroxide. If the heating is continued until the ammonia is mostly driven off, the litmus papers will then turn red, due to an excess of hydrogen chloride gas, which, dissolved in the moisture on the litmus paper, forms a hydrochloric acid solution. Thus, on vaporization, ammonium chloride is dissociated into two constituents, $NH_4Cl = NH_3 + HCl$, and the apparent molecular weight is the mean of that of the two components of the vapor.

The dissociation of electrolytes is, then, similar to the dissociation of gases in that it consists of a splitting up of molecules into smaller individuals. A full appreciation of its nature can, however, be obtained only in connection with a study of the chemical activity and the electrical conductivity of electrolytes.

9. It is evident, then, from the foregoing statements that the phenomena of the lowering of the freezing point, raising of the boiling point, and of osmotic pressure, as exhibited by solutions of electrolytes and non-electrolytes, all point to the same conclusion, namely, that the molecules of electrolytes, as ordinarily expressed by their chemical formulas, are dissociated into a greater number of smaller individuals, while the molecules of non-electrolytes are not so dissociated.

CHEMICAL ACTIVITY

10. As a rule, chemical reactions between electrolytes take place with great rapidity, while reactions involving a non-electrolyte take place only slowly. For example, solutions of silver nitrate and sodium chloride both conduct electricity. If they are mixed, there is instantly formed a precipitate of silver chloride, a white, insoluble substance, according to the reaction $AgNO_3 + NaCl = NaNO_3 + AgCl$.

A solution of chloroform, $CHCl_3$, is a non-conductor. If this solution is mixed with a solution of silver nitrate no precipitate of silver chloride is formed at first, and it is only after long standing that one slowly appears. It is reasonable to assume that there is in all cases a tendency for silver and chlorine atoms to unite. Whether or not this union will take place readily depends upon the state in which these atoms exist. If they are both in the condition of ions, then there is no obstacle to prevent an immediate combination; but if, on the other hand, one or both are already more or less firmly bound as part of undissociated molecules, then, in order for them to combine with each other, they must first be torn apart from the molecules in which they exist. That chloroform is only with difficulty dissociated to yield chlorine ions is evident, both from the fact that it does not conduct electricity and that it shows no immediate reaction with silver nitrate.

ELECTROLYTIC CONDUCTION

11. **Polarity in Chemical Compounds.** — A conception which has always been associated with the existence of chemical compounds since they were first systematically studied is that of polarity. Chemical polarity in compounds is certainly closely related to electrical polarity, if, indeed, there is any distinction. For example, in the compound sodium chloride, sodium is the positive constituent, chlorine the negative, as becomes evident when a current of electricity is passed through this electrolyte, either when dissolved in water or when in the molten condition. If the fused salt is used, its constituents, sodium and chlorine, collect at the two electrodes respectively, and since sodium is attracted to the negative electrode, or cathode, it must be the electrically positive constituent of the electrolyte. As chlorine, on the other hand, collects at the positive pole, or the anode, it must be the electrically negative constituent. Since the two constituents accumulate at opposite extremes of the body of liquid sodium chloride, there must have been throughout the liquid a movement of sodium toward the cathode and of chlorine toward the anode.

Again, if an electric current is passed through an aqueous solution of hydrochloric acid, hydrogen is liberated at the cathode and chlorine at the anode. Pure water does not conduct electricity, neither does dry, gaseous hydrogen chloride. But gaseous hydrogen chloride consists only of the undissociated molecules HCl, while experiments such as have been already mentioned show that the molecules of hydrochloric acid in aqueous solution are divided into the smaller individuals H and

Cl. In view of the fact that a current is only found to pass through a solution when accompanied by a movement in opposite directions of particles which are known to possess opposite polarity, it is plain that it must be these particles which carry the current. Thus, in the solution of hydrochloric acid the movement of hydrogen particles, which possess positive electrical charges, in the direction towards the cathode, and of chlorine particles, which possess negative charges, in the direction toward the anode, constitutes the actual movement of electricity, and it is this which, in fact, is the current.

12. **Ions.** — The apparent anomaly that molecules of sodium chloride are dissociated into sodium and chlorine atoms, each of which exist separately as physical molecules, but without any of the well-known properties of sodium and chlorine becoming manifest, may now be readily explained. When the original molecule is dissociated upon solution in water its two atoms become possessed of equal and opposite charges of electricity, the sodium atom taking the positive charge and the chlorine the negative.[1] These charged atoms, each having a separate existence, are called *ions*. The electrical charges are of great magnitude, and so affect the character of the ions as to account for the vast difference in their properties as compared with the atoms of the electrically neutral elements.

An ion, according to the electrolytic dissociation theory, is, then, a simple atom, or group of atoms, forming in itself a complete individual, and possessing a charge of electricity; and ions may be produced by the dissociation of larger electrically neutral molecules (that is, of the molecules of compounds as ordinarily expressed by their chemical formulas) into smaller ones bearing, respectively, *equivalent* amounts of positive and negative electricity. In every solution the aggregate of charges on the positive ions which it contains must be exactly equalized by the sum of the charges on the negative ions present, otherwise the solution as a whole could not be electrically neutral.

The cause of the phenomenon of ionization is not at all fully understood. In the case of melted salts it is probable that heat, by increasing the velocity with which the atoms of a molecule vibrate, separates them to such an extent that they no longer exist as molecules, but as ions, which are to a certain extent independent of each other. In the case of solutions, it is apparently some specific power possessed by the solvent by virtue of which it is able to so force itself in between the parts of the molecules as to separate them into ions. Different solvents vary very greatly in the extent to which they possess this power. The maximum among common solvents is reached in the case of water, while with some others it appears to be entirely lacking, as is illustrated by the experiments on page 77.

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[1] Since equal quantities of opposite kinds of electricity entirely neutralize each other, it is immaterial whether we regard the original undissociated molecule as possessing no electrical charges, or as already possessing opposite charges which neutralize each other in such a manner that the molecule behaves as if uncharged.

When electrodes, connected with a battery or a dynamo, are inserted in a solution of hydrochloric acid, the hydrogen ions, by virtue of their positive charges, are attracted to the negative electrode; these ions, when they touch the electrode, give up their electrical charges, neutralizing the negative electricity on the electrode, and then become ordinary hydrogen atoms, which, in turn, unite in pairs to form hydrogen molecules, and thus hydrogen gas escapes at the cathode. In an exactly similar manner negative chlorine ions are attracted to the anode, where they give up their charges of electricity. They thus become neutral chlorine atoms, which, combining in pairs, form the molecules of the chlorine gas which escapes.

13. As already stated, the electrical charges on the positive and negative ions of an electrolyte must just equalize each other. Figure 1 represents a solution in which ten of each kind of ions are pictured, instead of the almost countless number which are in reality present in the solution. It is assumed, at the start, that the charge on each positive ion in the upper row is equalized by the charge on the negative ion just below it.

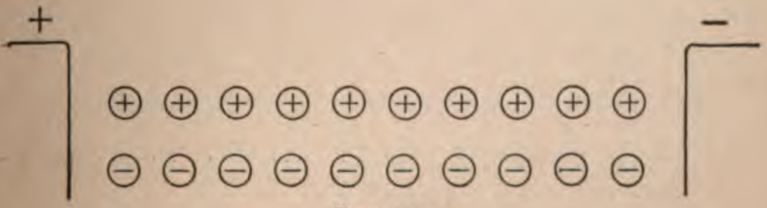

FIGURE 1

If the electrodes + and − are charged, as represented in the diagram, from a dynamo or battery, the negative ion farthest to the left is attracted to the positive electrode, where it parts with its charge, which neutralizes some of the positive electricity on that electrode. This would leave the first positive ion at the left unneutralized by the opposite charge of any other ion, and it is at once repelled by the positive electrode and moves toward the right, while at the same time the second negative ion, being attracted by it, moves toward it until the two have come sufficiently close together to equalize each other. The second positive ion, being now unbalanced, attracts the third negative ion until these two equalize each other; and so on, until the ninth positive ion and the tenth negative ion, after neutralizing each other, leave the tenth positive ion to be attracted to the negative electrode, there to give up its charge and neutralize a part of the negative electricity on that electrode. Then the solution is left in the condition represented in Figure 2. At the surface of each electrode is the discharged ion, which is now an electrically neutral particle.

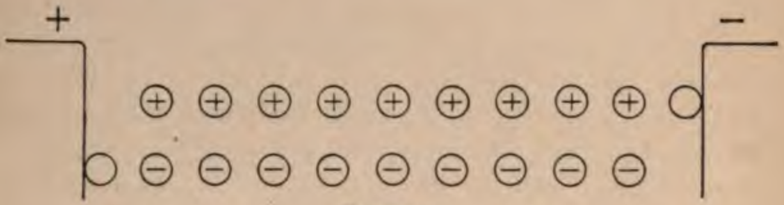

FIGURE 2

The further behavior of the discharged ions will be spoken of in Section 16. It should be noted that the solution is now in the same condition as at the start, but with one less pair of ions, and the process just described is ready to be repeated. In an actual case of electrolysis, where the ions are present in enormous numbers, this procedure repeats itself with almost infinite rapidity.

14. **Movement of the Ions.** — That ions do actually move through a solution may be most easily shown in the case of some electrolyte both ions of which are colored, so that their motion through the liquid is made visible.

This may be demonstrated as follows: In the lower bend of a U-tube (Figure 3) is poured some fairly concentrated solution of copper bichromate, $CuCr_2O_7$.[1] This salt in aqueous solution is dissociated into positive Cu-ions, which are blue, and negative Cr_2O_7-ions, which are yellow. The resultant color is green. On top of this solution a lighter solution of sodium chloride is so cautiously poured as to avoid mixing the layers. Platinum electrodes are inserted in the two arms of the tube, and a current is passed through the entire liquid. After about twenty minutes there will have appeared just above the green liquid a blue zone of Cu-ions on the side toward the cathode and a yellow zone on the side toward the anode, both zones being perhaps 2 cm. high. The blue zone is caused by the movement of blue Cu-ions upward from the original boundary between the two liquids, as well as the movement of the yellow Cr_2O_7-ions downward, leaving only the blue of the Cu-ions. The yellow zone in the other arm of the tube also appears above and below the original boundary. It should be noted that after the Cu-ions and Cr_2O_7-ions have moved into the colorless liquid their electrical charges are still balanced, but it is now brought about by the opposite charges on the Cl- and Na-ions, respectively, which are derived from the sodium chloride.

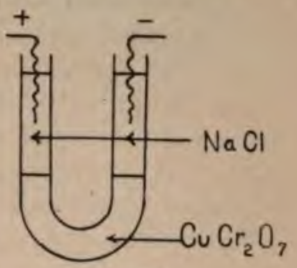

FIGURE 3

The change in position of the boundary between the blue or yellow and the colorless liquids in the above experiment is not rapid,[2] and the slowness of this motion is due to the great friction offered by the solvent to the motion through it of particles as minute as the ions. This will be understood if it is recalled that while a small fragment of chalk will drop rapidly to the floor under the influence of gravity, yet if the same quantity of chalk is suspended in the air in the form of chalk dust, as may be brought about by striking together two blackboard erasers, a long time is required for the chalk dust to settle to the floor, although in the latter case the force of gravity is just as great as in the former.

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[1] For the details of this experiment arranged for lecture demonstration, see *Jour. Am. Chem. Soc.*, **22**, p. 729.

[2] If the distance between the electrodes is 100 cm., and the difference of potential between them is 100 volts, the boundary lines would move about 2.5 cm. in an hour. This is about the average rate of motion of an ion through a solution where the electrical potential is 1 volt for each centimeter of distance between the electrodes. Hydroxyl ions, however, move with about three times, and hydrogen ions with about six times, this velocity.

15. **Electrical Charges upon the Ions.** — In view of the statement just made concerning the slowness with which the ions move during electrolysis, it may appear remarkable that electrolytes should convey the current as readily as they are known to do. The explanation of this fact is found in the magnitude of the charge which each ion bears. This is so large that, notwithstanding the sluggishness of the motion of the ions, a sufficient quantity of electricity is brought by the small number of them which do reach each electrode in a given interval of time to constitute a considerable current.

As has already been briefly noted, a solution of an electrolyte gives no external evidence of being electrified, such, for example, as is shown by a stick of sealing wax which has been rubbed with a cat's skin; that is, it does not attract or repel light bodies which are brought near it. It cannot, therefore, contain an excess of either positive or negative electricity. Since, however, the ions *are* assumed to carry charges, it must follow that with any electrolyte the charges upon the opposite ions must be exactly equivalent in amount, so that their separate effects are equalized within the solution. If the charge which the hydrogen ion bears be taken as the unit quantity of positive charge, then the chlorine ion must bear one unit of negative charge, since hydrochloric acid gives equal numbers of hydrogen and chlorine ions: —

$$HCl \longrightarrow H^+ + Cl^-.$$

From the same reasoning, it appears that the sodium ion must bear one unit of positive electricity, and the calcium ion two units: —

$$NaCl \longrightarrow Na^+ + Cl^-;$$
$$CaCl_2 \longrightarrow Ca^{++} + Cl^- + Cl^-.$$

It should be noted that, in general, the number of unit charges which an ion bears is the same as the valence of the atom, or atom group, from which the ion is formed. A few of the most common ions with the number of units of positive or negative charges which they carry are given in the following table: —

H^+	Na^+	K^+	Ag^+	$(NH_4)^+$		
Cl^-	Br^-	I^-	$(NO_3)^-$	$(ClO_3)^-$	$(CN)^-$	$(C_2H_3O_2)^-$
Ca^{++}	Ba^{++}	Cu^{++}	Zn^{++}	Cd^{++}	Pb^{++}	Fe^{++}
S^{--}	$(SO_4)^{--}$	$(Cr_2O_7)^{--}$				
Fe^{+++}	Al^{+++}		PO_4^{---}	$(Fe(CN)_6)^{---}$		
$(Fe(CN)_6)^{----}$						

16. **Reactions at the Electrodes.** — In Section 13 the process has been described by which the current is carried through a solution as a result of the movement of ions toward the electrodes, where these ions give up their electric charges. The further behavior of the discharged ions is something in no wise connected with the conditions of their movement before they were discharged.

One of the simplest cases is that of the electrolysis of a concentrated hydrochloric acid solution. The ions in such a solution, upon being discharged, become simply electrically neutral atoms, which at this moment are in the so-called nascent state, and are chemically exceedingly active. Indeed, free uncharged atoms of chlorine or hydrogen are not capable of continued independent existence; if no other body is present with which they can unite, they themselves combine in pairs to form the chemically much less active molecules of chlorine and hydrogen. These molecules then escape from the liquid at the two electrodes in the form of chlorine gas and hydrogen gas.

17. Another typical case is that of the electrolysis of a salt of a heavy metal between electrodes of the same metal. In a copper sulphate solution the ions which bear the current are Cu^{++} and SO_4^{--}. If copper electrodes are immersed in such a solution, the positive electricity is given up at the cathode by the Cu^{++}-ions, which thus become Cu-atoms and simply add themselves to the mass of metal of the electrode. The SO_4^{--}-ions about the cathode are then, being electrically unbalanced, repelled by the cathode toward the anode, around which they collect. Here, instead of giving up their electric charges, they find these charges equalized by those on the Cu^{++}-ions which are produced from neutral Cu-atoms of the material of the copper anode, since it is by the formation of these positive ions out of the mass of the electrode that the current enters the solution.

In a case of this kind, the fact that an almost infinitesimal electrical potential[1] is sufficient to cause some current to pass through the solution again strongly supports the idea that electrolytes are already dissociated into ions even before a potential is applied. If this were not the case, no current would pass until a certain definite potential were reached sufficient to pull the molecules apart, when the current would suddenly begin to flow.

18. It is frequently true that the products set free at the electrodes give no direct indication as to the ions which conduct the current through the solution. This is illustrated by the electrolysis of a solution of potassium sulphate between platinum electrodes. The ions which transmit the current are K^+K^+ and SO_4^{--}, but the products set free are the gases hydrogen and oxygen. Furthermore, the solution at the cathode becomes alkaline, while that at the anode becomes acid. These facts may be partially explained by assuming that the K^+-ions on reaching the cathode give up their charges and become electrically neutral K-atoms, which then react with water to produce hydrogen gas and potassium hydroxide; the SO_4^{--}-ions on reaching the anode are discharged and, not being capable of existence alone in the uncharged condition, then react with water with the formation of oxygen gas and sulphuric acid. A more complete as well as a probably more exact explanation is possible, however, if the Principle of Mass Action, together with the fact that water itself is slightly dissociated, is taken into consideration. (See page 50.)

19. A comprehension of the magnitude of the charges of electricity which are carried by the ions can be obtained from the following statements regarding the amount of electricity, the passage of which through the solution of a metallic salt, between electrodes of the same metal, is accompanied by the dissolving from the anode and depositing upon the cathode of an equivalent weight[2] in grams of the metal, for example, 31.5 grams of copper. This amount of electricity, if forced through a 50 candle power incandescent lamp, would keep it lighted at its full brilliancy for 13.5 hours. If the positive electricity discharged at the cathode by 31.5 grams of Cu^{++}-ions could be condensed upon a metal sphere, and if the negative electricity produced upon the anode, as a result of the taking away of the 31.5 grams of positive

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[1] That is, electrical pressure.

[2] Since the copper ion carries a double charge of electricity, one-half an atomic weight (or 31.5 grams) of copper is equivalent to a whole atomic weight of any element whose ion carries but a single charge.

Cu^{++}-ions formed, could be condensed upon another metallic sphere, and if these charged spheres could be held with their charges upon them at a distance of 3 feet apart, the attraction pulling them together would be equal to a force of 10^{16} tons.

SUMMARY

20. The conclusions drawn from the discussions in this chapter may be summarized as follows: Solutions have been studied from five standpoints, namely, with reference to freezing point, to boiling point, to osmotic pressure, to chemical activity, and to electrical conductivity, and in each case it appears that the properties exhibited by the solutions are dependent upon the presence of the dissolved substance and its condition within the solution. With respect to this condition it is at once evident that *any* substance, when dissolved to form a homogeneous mixture with the solvent, must necessarily be subdivided into very small particles, which may, however, be either larger or smaller than, or identical with, the chemical molecules. Of the properties enumerated, three, namely, freezing point, boiling point, and osmotic pressure, are influenced only by the number of these particles present in the solutions, and not by their size or chemical character.

A quantitative study of the three properties just enumerated has shown that the extent of the subdivision within the solution varies with different classes of substances. Non-electrolytes, in general, when dissolved in water yield particles which are identical with those designated as chemical molecules; that is, with those which correspond to the usual chemical formulas. For example, ethyl alcohol, C_2H_6O; sugar, $C_{12}H_{22}O_{11}$; urea, CON_2H_4.

Electrolytes, on the other hand, yield a number of individual particles which is greater than that possible if only the chemical molecules are considered. This leads directly to the conclusion that some or all of these molecules undergo further subdivision into smaller molecules, which, however, produce the same physical effect as the chemical molecules, and to which the name ions is given. But it is also found that it is only those bodies which, in solution, yield these ions that transmit the electric current and exhibit marked chemical activity; and a consideration of these properties has not only confirmed the assumed independent existence within the solution of these parts of the chemical molecules, but it has also indicated that each of these ions carries an electrical charge of very considerable magnitude.

If the foregoing conclusions, which are in accordance with the Electrolytic Dissociation Theory as proposed by Arrhenius, are well established, it should be found that the values for the degree of ionization of a given substance in solution, determined from an independent study of such of the different properties of the solution as admit of quantitative measurement, should agree. The following table shows that these values for certain well-known electrolytes are concordant, the small variations being satisfactorily accounted for, by what are known as unavoidable, experimental errors. In accordance with a well-established custom, the number of mols into which one chemical mol is dissociated is designated as *i*. The second column of the table shows the molal concentration of the salt at which the value is determined.

Salt.	Molal conc'n.	VALUES OF *i* DETERMINED FROM		
		Osmotic pressure.	Freezing point.	Electrical conductivity.
KCl	0.14	1.81	1.86	1.86
$Ca(NO_3)_2$	0.18	2.48	2.47	2.46
$K_4(Fe(CN)_6)$	0.356	3.09	. .	3.07
$MgSO_4$	0.38	1.25	1.20	1.35
LiCl	0.13	1.92	1.94	1.84
$SrCl_2$	0.18	2.69	2.52	2.51
$CaCl_2$	0.1	2.47	2.65	2.48
Succinic acid, $H_2C_4H_4O_4$	0.1	. .	1.07	1.03
Acetic acid, $HC_2H_3O_2$	0.1	. .	1.019	1.013
NH_4OH	0.05	. .	1.038	1.022

CHAPTER II

THE LAW OF MASS ACTION AND THE CHEMICAL BEHAVIOR OF ELECTROLYTES

REVERSIBLE REACTIONS AND THE EFFECT OF MASS

21. In order to understand the applications of the Law of Mass Action, it is first necessary to know what is meant by a reversible reaction. A familiar example is to be found in the action of steam upon iron filings. If iron filings are introduced into a tube and brought to a high temperature, and steam is then passed over them, the iron will be changed to iron oxide, and hydrogen will be liberated according to the reaction $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$. If, however, the tube is kept at the same temperature and hydrogen is passed through instead of steam, the iron oxide will be reduced to iron, $Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$; that is, the first reaction is reversed.

It should be noted that in the first of these two cases the steam is supplied freely, and the hydrogen, which is the product of the reaction, is forced out of the tube, while in the second case the ready supply of hydrogen displaces the steam which is formed from the reduction of the iron oxide.

Suppose, however, that the conditions are so altered that the gaseous product of the reaction cannot escape, as would be the case if the reactions were carried out in two sealed tubes, one of which had been previously charged with iron and water vapor, the other with iron oxide and hydrogen. If these tubes were heated the reaction in each would begin as described above for the open tube; but in the first tube the amount of water vapor would gradually diminish and that of the hydrogen increase, while in the second the concentration of the hydrogen would diminish as that of the water vapor increased. It is easy to see that a point would be reached in each at which the accumulation of the body which was the *product* of the initial reaction might be sufficient to cause a reversal of the process to take place. In fact, experiment has shown that, under the conditions cited, the reaction in each tube apparently ceases at a definite point, and that when this point has been reached the ratio of the concentration of hydrogen and water vapor is the same in both tubes. This is called the point of *equilibrium*. Instead, however, of regarding this condition of equilibrium as one at which chemical action has ceased, it is better to assume that both reactions are still taking place, but that by them as many H_2- as H_2O-molecules are being produced in a given interval of time, so that the relative amounts present from moment to moment no longer change. Such a condition may be represented by the equation $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$, where all four substances continue to exist in equilibrium with each other.

22. From the preceding statements it is evident that the direction in which a reversible reaction will proceed is determined by the relative quantities of the reacting substances which are present in a given volume, that is, upon their relative concentrations. This is, however, in effect a statement of the principle of the *Law of Mass Action*, which may be concisely formulated as follows: —

The rapidity of a chemical change is proportional to the concentrations of the substances taking part in the reaction.

Of the many cases in which this principle will find application in the remaining pages, nearly all will represent conditions of equilibrium in reversible reactions where the velocities of the opposing reactions are equal, as described above for iron, steam, iron oxide, and hydrogen.

The law may be restated, with special reference to such conditions, as follows: —

If, in a confined system, certain substances are present which, by reacting with one another, produce certain new substances, and these, in turn, react to reproduce the original substances, it is found that, whatever the actual amounts of all the reacting bodies, the final concentrations when equilibrium is reached always bear such a relation to each other that the product of the concentrations of the first set of substances stands in a definite numerical ratio to the product of the concentrations of the second set.

To illustrate: If the substances A and B react to form the substances C and D according to the chemical reaction $A + B = C + D$, into which only one molecule of each body enters, then whenever these four bodies exist together in a confined volume in a state of equilibrium, the ratio of their concentrations may be expressed as follows: —

$$\frac{Conc'n\ A \times Conc'n\ B}{Conc'n\ C \times Conc'n\ D} = Constant,$$

where *Constant* is a definite numerical quantity characteristic of this reaction.

23. It will be noticed that the actual reversible reaction considered in Section 21 is not so simple as the ideal one just formulated, and it is also complicated by the fact that two of the reacting bodies, iron oxide and iron, are solid, while the others are gaseous. The nature of the experimental justification for the Mass Action Law may be more satisfactorily and, indeed, very beautifully demonstrated by a study of the reversible reaction involving the dissociation and reassociation of hydrogen iodide at high temperatures.

At room temperatures any given volume of hydrogen iodide gas may be considered to consist only of molecules corresponding to the symbol HI. If, however, a confined volume of this gas is subjected to increasing temperatures, it is found that at 180° C., and above, it undergoes a gradual dissociation into hydrogen gas and iodine vapor, according to the equation $2HI = H_2 + I_2$, and temperatures may easily be reached at which this dissociation is practically complete. If now the temperature is allowed to sink slowly there is a gradual reassociation of the hydrogen and iodine to form hydrogen iodide; and, moreover, if the composition of the gaseous mixture is determined at any definite temperature during the heating process, and again at the same temperature during the cooling process, the relative amounts of iodine, hydrogen, and hydrogen iodide are found to be the same, provided that in either case the temperature is held at this point for a sufficient length of time to permit a state of equilibrium to become established. It is also true that equivalent amounts of hydrogen and iodine, if heated to a given temperature, will yield a mixture of the three gases identical in composition with that obtained by starting with hydrogen iodide.

Experiment has shown that if equivalent amounts of hydrogen and iodine are heated to 445° C. in a sealed vessel, by placing it in the vapors of boiling sulphur, 79 per cent. of these gases unite to form hydrogen iodide. On the other hand, if hydrogen iodide is heated in a similar manner approximately 21 per cent. is decomposed into hydrogen and iodine.

The changes which take place within the gaseous mixture may be pictured somewhat as follows: When the mixture of hydrogen and iodine is suddenly heated to 445° it contains, at the first moment, no hydrogen iodide. This body can only form when hydrogen molecules and iodine molecules collide with each other, and even then it is necessary for them to collide with such a velocity and in such a manner that their atoms shall be so far separated by the shock that, instead of returning to their former relative positions, they can recombine to form different molecules. The conditions requisite for this are established as the temperature of the gas increases, and a certain definite percentage of the collisions of the different molecules will result in such an interchange of atoms, this percentage depending, in general, both upon the temperature and upon the chemical nature of the atoms and molecules concerned. As the number of HI-molecules increases the number of H_2- and I_2-molecules must decrease, consequently the number of collisions between the latter must also decrease, and the amount of hydrogen iodide which is formed in a given interval of time must be diminished accordingly. In other words, the amount of hydrogen iodide formed in a unit time (that is, the velocity of the reaction) depends upon the number of hydrogen and iodine molecules in a unit volume, or, more exactly stated, it is proportional to the concentration of H_2-molecules multiplied by the concentration of I_2-molecules. Representing the velocity of this reaction by V_I, it is true that

$$V_I = \mathit{Conc'n}\ H_2 \times \mathit{Conc'n}\ I_2 \times \mathit{Constant}_I,$$

where $\mathit{Constant}_I$ is a definite numerical quantity depending on the temperature and upon the nature of this particular reaction, or, in other words, upon the percentage of the collisions of H_2- and I_2-molecules which result in the formation of HI-molecules.

Again, when hydrogen iodide is suddenly heated to 445°, HI-molecules can only decompose when two of them collide in such a way that both will be sufficiently broken apart for a recombination of atoms into the molecules H_2 and I_2 to take place. The velocity of this reaction, since two molecules of HI are involved, will be

$$V_{II} = \mathit{Conc'n}\ HI \times \mathit{Conc'n}\ HI \times \mathit{Constant}_{II},$$

or

$$V_{II} = (\mathit{Conc'n}\ HI)^2 \times \mathit{Constant}_{II}.$$

As the amounts of hydrogen and iodine increase, the amount of hydrogen iodide, and with it the velocity of Reaction II, decreases. Reaction I must begin to take place and constantly increase in velocity until 21 per cent. of the hydrogen iodide has been converted into hydrogen and iodine. At this point there is no further change in concentrations, and the velocities of the two reactions are equal, a condition similar to that already described in the case of the hydrogen and steam. These are the conditions of equilibrium, and since under those conditions V_I and V_{II} are equal, the equivalent expressions must also be equal:—

$$\mathit{Conc'n}\ H_2 \times \mathit{Conc'n}\ I_2 \times \mathit{Constant}_I = (\mathit{Conc'n}\ HI)^2 \times \mathit{Constant}_{II},$$

or

$$\frac{\mathit{Conc'n}\ H_2 \times \mathit{Conc'n}\ I_2}{(\mathit{Conc'n}\ HI)^2} = \frac{\mathit{Constant}_{II}}{\mathit{Constant}_I} = \mathit{Constant}.$$

This equation shows the relative amounts of the different reacting substances in a given volume (for example, 1 liter) which must be present when the point of equilibrium is reached, and is a mathematical expression of the principle stated as the Law of Mass Action.

24. It is probable that all chemical reactions are to some extent reversible, and are therefore governed by this law, which thus becomes one of the most important principles underlying chemical changes. It is true that the extent to which many reactions are reversible, under conditions which usually prevail, is so small as to be practically negligible; but others, as illustrated above, may be reversed with comparative ease. Every instance of the dissociation of an electrolyte into its ions is such a reversible reaction, and the following sections are devoted to a discussion of the applications of the Law of Mass Action to certain familiar and typical instances of chemical change.

DEGREE OF IONIZATION

25. It has just been stated that every instance of the dissociation of an electrolyte into its ions is a reversible reaction. For example, when sodium chloride is dissolved in water the condition of equilibrium which results is represented by the equation $NaCl \rightleftharpoons Na^+ + Cl^-$.

From measurements of the freezing point and of the electrical conductivity it is known that in a solution of sodium chloride containing 0.1 chemical mol to the liter, 90 per cent. of the salt molecules are dissociated into ions, while 10 per cent. remain in the undissociated condition. If, however, the volume of the solution in which this amount of the salt is dissolved is varied, then the percentage of the salt which is dissociated will not remain the same, as is evident from a consideration of a mathematical expression of the Mass Action Law as applied to this case, namely,

$$\frac{\textit{Conc'n}\ Na^+ \times \textit{Conc'n}\ Cl^-}{\textit{Conc'n}\ NaCl} = \textit{Constant.}$$

For, in case the total concentration of the salt were doubled, as may be accomplished by evaporating away one-half of the water, then the concentrations of all of the three bodies Na^+, Cl^-, and NaCl would be doubled, if it were assumed that no change in the percentage ionization occurred. Under these conditions the numerator of the fraction would be increased four times while the denominator would be increased but twice, thereby doubling the value of the fraction — a condition which is impossible according to the Law of Mass Action, since the value of the fraction must remain constant. In order that it may remain constant, it is necessary that the concentration of NaCl shall increase by a greater amount than that of either Na^+ or Cl^-; that is to say, that some of the ions shall combine to form undissociated salt, and the percentage of such molecules will, therefore, be greater than the initial 10 per cent.

If the total concentration of the salt is diminished, as may be accomplished by diluting with pure water, it is evident from a similar process of reasoning that more of the undissociated molecules must dissociate, and consequently the percentage of ionization must increase.

The principle just illustrated holds true for solutions of all electrolytes, namely, that with increasing dilution the *percentage* ionized increases (although, of course, the actual *concentration* of the ions must decrease), while with increasing concentration the *percentage* ionization decreases.

THE FORMATION OF INSOLUBLE COMPOUNDS THROUGH THE INTERACTION OF CERTAIN IONS

26. When solutions of two or more electrolytes are mixed the ions which they contain at once enter into new combinations, with the formation of larger or smaller amounts of undissociated molecules not found in either of the original solutions. Whether or not this rearrangement of the constituents of the solution is at once made evident to the observer will usually depend upon the solubility of the new compounds which may have resulted. For example, in separate solutions of sodium chloride and potassium nitrate the ions of each salt are in equilibrium with the undissociated molecules of the respective compounds, as expressed by the equations: —

$$NaCl \rightleftharpoons Na^+ + Cl^-;$$
$$KNO_3 \rightleftharpoons K^+ + NO_3^-.$$

If now these two solutions are mixed, a certain number of undissociated molecules of two new salts will be formed, and this interchange will continue until new conditions of equilibrium are established as expressed by the equations: —

$$K^+ + Cl^- \rightleftharpoons KCl;$$
$$Na^+ + NO_3^- \rightleftharpoons NaNO_3.$$

In this particular instance the observer will discover no evidence that any such change has occurred, and, indeed, the actual change is of little magnitude, because, first, the new compounds, potassium chloride and sodium nitrate, as well as the original salts, sodium chloride and potassium nitrate, are strong electrolytes, and hence largely ionized; and, second, because all are very soluble bodies, and therefore remain in solution.

27. On the other hand, if any new combination of ions can result in the production of an *insoluble* body, the resulting changes may be of much greater magnitude. For example, in solutions of potassium chloride and silver nitrate, taken separately, a condition of equilibrium exists between their undissociated molecules and ions, in which, as in the cases cited in the previous paragraph, the ions very largely predominate. If, however, these solutions are mixed, a combination both of Ag^+-ions with Cl^--ions to form undissociated silver chloride, and of K^+-ions with NO_3^--ions to form undissociated potassium nitrate, becomes possible; and, since the silver chloride is almost completely insoluble, the moment that any of this compound is formed it separates from solution in the form of a precipitate. In this way precipitation will continue till either the Ag^+- or Cl^--ions, or both, are used up, because silver chloride, being insoluble, cannot remain in solution in the undissociated form in sufficient quantity to maintain equilibrium with any appreciable quantity of its ions.

28. The remaining solution contains K^+- and NO_3^--ions, with but a very small proportion of undissociated KNO_3. If this solution is filtered from the precipitate and evaporated until an insufficient quantity of water is left to keep the undissociated potassium nitrate in solution, this salt then separates as crystals from the solution. It is to be noted that this separation is entirely comparable with the precipitation of the silver chloride just described, the difference in their manner of formation being wholly due to the difference in their solubilities.

It may be stated as a general rule, which has but very few exceptions, that salts in solution are largely dissociated into their ions. This being true, it is evident that there will be but slight chemical change whenever solutions of salts are mixed, unless one of the new salts which may be formed by the mixture is very little soluble.

SOLUBILITY PRODUCT

29. When any pure, solid substance is brought into contact with a liquid in which it is soluble, its molecules immediately begin to pass from its surface into the liquid, much as the molecules of a gas pass into a vacuous space, or the molecules of a liquid, as water, pass into the atmosphere when it evaporates. This process continues, if the solid is present in sufficient quantity, until a solution results which is saturated with the solid at the temperature employed. Under the conditions then prevailing the molecules of the solid still continue to pass into the solvent liquid, but molecules are also returning from the solution to the solid, and the number passing in each direction has become exactly equal. Consequently there are no further changes in concentration of the solution, and a condition of equilibrium exists between the solid and its dissolved molecules. The amount of any substance which has dissolved to form a saturated solution is always a definite quantity for a given temperature, and is characteristic of that particular substance. It may be expressed as the number of grams which are dissolved in a liter of solution.

A non-electrolyte, such as sugar, dissolves in water solely in the form of undissociated molecules until these have reached the saturation concentration, when they are in equilibrium with solid sugar. An electrolyte also dissolves as undissociated molecules at first, and when the solution is saturated these undissociated molecules will be in equilibrium with the solid salt, and will have a certain definite concentration, just as the molecules of undissociated sugar had a certain definite concentration when in equilibrium with the solid sugar. But the case of the electrolyte is further complicated because its molecules, as, for example, those of silver bromate, as soon as they dissolve dissociate for the most part into ions, whereby the concentration of the un-ionized molecules would be diminished were it not for the fact that more solid salt at once dissolves until the equilibrium is reëstablished. When, therefore, solid silver bromate is suspended in water it will dissolve until that concentration of the silver bromate molecules is reached which stands in equilibrium with the solid, and also until that concentration of the silver and bromate ions is reached which stands in equilibrium with the undissociated molecules. This is expressed by the equation:—

$$\mathbf{AgBrO_3} \rightleftharpoons \mathrm{AgBrO_3} \rightleftharpoons \mathrm{Ag^+} + \mathrm{BrO_3^-}.$$

The relation between the concentrations of the ions and molecules in the solution may be expressed according to the Mass Action Law as follows:—

$$\frac{\mathit{Conc'n}\ \mathrm{Ag^+} \times \mathit{Conc'n}\ \mathrm{BrO_3^-}}{\mathit{Conc'n}\ \mathrm{AgBrO_3}} = \mathit{Constant}_1,$$

or

$$\mathit{Conc'n}\ \mathrm{Ag^+} \times \mathit{Conc'n}\ \mathrm{BrO_3^-} = \mathit{Constant}_1 \times \mathit{Conc'n}\ \mathrm{AgBrO_3}.$$

Since in a *saturated* solution the concentration of undissociated silver bromate is always the same, the value of *Conc'n* $\mathrm{AgBrO_3}$ is also a constant quantity, and the relation expressed above may be simplified to

$$\mathit{Conc'n}\ \mathrm{Ag^+} \times \mathit{Conc'n}\ \mathrm{BrO_3^-} = \mathit{Constant};$$

that is to say, in a saturated solution of silver bromate the concentration of the silver ions multiplied by the concentration of the bromate ions is equal to a definite quantity. This quantity is called the *solubility product* for silver bromate. The general application of this principle may be stated as follows: In a saturated solution of any electrolyte the product of the concentrations of its ions has a certain definite value, which is known as the *solubility product* for that substance.[1] If this value is exceeded the solution is supersaturated, and some of the solid substance must separate from the solution. If this value has not been reached more of the solid substance can dissolve.

30. The wider significance of the solubility product becomes evident from the behavior of a saturated salt solution when other salts are dissolved in it. Thus, if some crystals of a soluble salt, such as sodium nitrate, which gives no ion in common with silver bromate, are dropped into a solution of that salt and stirred about, there will be no change noticed except that the added salt dissolves with the same readiness as in pure water. If, on the other hand, crystals of silver nitrate, a salt which does have an ion in common, are used, they dissolve as in pure water, but immediately following their solution there separates out all through the solution a finely crystalline precipitate of silver bromate. Crystals of potassium bromate, when dissolved, also produce an exactly similar precipitation of silver bromate. This may be explained as follows: In the saturated solution containing only silver bromate the concentration[1] of both the Ag^+- and BrO_3^--ions is the same, and their product is the solubility product. The value of this product is in no wise altered by the presence in the solution of moderate amounts of other indifferent ions. But when, with the addition of silver nitrate, an excess of Ag^+-ions is brought into the solution, the product of the concentrations of the ions is increased beyond the solubility product; that is, the solution is supersaturated, and the product can only be brought back to its normal value by the disappearance of Ag^+- and BrO_3^--ions together, as they unite to form the undissociated salt. Since, because of its slight solubility in water, only a very small amount of the latter can exist in solution, it continues to separate in the solid state as fast as it is formed. If, for example, sufficient silver nitrate has been added to make the final concentration of Ag^+-ions ten times as great as at the start, then only one-tenth of the original BrO_3^--ions can remain in the solution. If instead of Ag^+-ions an excess of BrO_3^--ions is brought into the solution by the addition of potassium bromate, the concentration of the Ag^+-ions must be diminished through separation of the solid salt in an exactly similar way.

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[1] In the case of an electrolyte, the molecule of which yields more than one ion of a given sort, the concentration of that ion must be raised to a higher power, *e.g.*, $\mathrm{PbI_2} \rightleftharpoons \mathrm{Pb^{++}} + \mathrm{I^-} + \mathrm{I^-}$, and the solubility product becomes *Conc'n* $\mathrm{Pb^{++}} \times (\mathit{Conc'n}\ \mathrm{I^-})^2$.

Likewise when solid silver bromate is stirred into pure water, or solutions of silver nitrate or potassium bromate, it will dissolve only until the solubility product is reached, and the amount which can dissolve before this product is attained is naturally less in the last two cases than in the first, because of the previous existence within these solutions of Ag^+- or BrO_3^--ions. The few figures which follow, taken from actual experiments, are in entire agreement with the theory:—

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[1] By concentration, in such a case as this, is meant the number of equivalent weights in grams of the ions or salts in question, rather than the number of grams which are contained in a definite volume of the solution. For example, in a solution containing 108 grams of Ag^+-ions and 128 grams of BrO_3^--ions, the concentration of the two ions would be said to be the same, as these quantities represent an equivalent weight in each case.

Solubility of $AgBrO_3$ in pure water = 0.00810 molal.[1]
Solubility of $AgBrO_3$ in 0.0364 molal $KBrO_3$ = 0.00227 molal.
Solubility of $AgBrO_3$ in 0.0364 molal $AgNO_3$ = 0.00216 molal.

Characteristic Reactions of the Various Ions

31. **Simple Ions.** — It has already been stated, on page 27, that when a solution containing Ag^+-ions, such as a solution of silver nitrate, is mixed with one containing Cl^--ions, such as potassium chloride, these ions unite at once to form the characteristic compound, silver chloride, which, because of its insolubility in water, is thrown out of solution as a precipitate. Since this reaction always occurs when Ag^+- and Cl^--ions are brought together, it may be used to demonstrate the presence of either of these ions in a solution; and all substances, such as HCl, $NaCl$, $MgCl_2$, $AlCl_3$, etc., which yield Cl^--ions should cause this reaction. For example, if the addition of a solution of silver nitrate to another solution occasions the precipitation of a white, curdy substance, which turns dark on exposure to a strong light, then this substance is probably silver chloride and the solution contains Cl^--ions.

It is, of course, equally true that this reaction may be used as a test for Ag^+-ions by adding a solution of HCl, for example, to the solution suspected to contain the Ag^+-ions.

Moreover, it is possible to select reactions which are similarly characteristic of a large number of the ions; thus Ba^{++}-ions when brought into contact with SO_4^{--}-ions always yield a white precipitate of barium sulphate; Pb^{++}-ions when brought into contact with S^{--}-ions cause a black precipitate of lead sulphide to fall, and so on. These, as will be noted later, constitute the reactions upon which the systematic scheme of qualitative chemical analysis is based, as well as the procedures of quantitative analysis.

32. In the illustration of the application of the principle of the solubility product cited in Section 30, the salts which produced the increased concentration of the Ag^+- and BrO_3^--ions were assumed to be added to the solution in the solid form. A little reflection will show that if such salts are readily soluble in water, thus permitting the preparation of solutions which are highly

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[1] The solubility is here expressed as the number of chemical mols per liter (see also the previous footnote).

concentrated as compared with the solution of the slightly soluble silver bromate, the addition of these concentrated solutions would tend to produce a similar effect to that resulting from the addition of the solid salt, namely, to lessen the solubility of the bromate. The reagents used in qualitative and quantitative analysis are usually just such relatively concentrated solutions of various salts, and the substances which they precipitate are bodies of even less solubility than the silver bromate. It is easy, then, to understand that, in general, the test for such an ion as SO_4^{--} (or the quantitative measurement of that ion) by the addition of Ba^{++}-ions (precipitation of $BaSO_4$) may be made more delicate by the addition of a moderate excess of the reagent; that is, by increasing the concentration of the Ba^{++}-ions, thus rendering the separation of the $BaSO_4$ more complete.

33. **Complex Ions.** — Not all substances which contain chlorine or silver will, however, yield Ag^+- or Cl^--ions if tested as above described. The failure may be due, as in the case of chloroform, to the fact that no dissociation occurs, or it may be due to the formation within the solution of other than simple Ag^+- and Cl^--ions. For example, the salt silver ammonia nitrate can be obtained by adding an excess of ammonia water to a silver nitrate solution, $Ag^+, NO_3^- + 2NH_3 = (Ag.2NH_3)^+, NO_3^-$. This salt is undoubtedly ionized, but in such a way as to yield a complex ion which exhibits properties very different from those of simple Ag^+-ions, and does not combine with Cl^--ions to form an insoluble salt.

In a similar way complex anions may be formed, and some elements which, as simple ions, behave as cations may become a part of such anions. The salt potassium silver cyanide will serve to illustrate this.

As silver cyanide is insoluble, Ag^+-ions and CN^--ions when brought into the same solution cause a precipitate of AgCN to form. If, however, this precipitate is treated with an excess of potassium cyanide solution, the molecules of AgCN have the power of combining with CN^--ions in the solution to form a new complex ion. This, as well as the K^+-ions, is soluble, and the precipitate redissolves, $K^+, CN^- + \mathbf{AgCN} = K^+, (Ag(CN)_2)^-$.

That the silver is a constituent of the positive ion of silver ammonia nitrate and of the negative ion of the potassium silver cyanide is shown by the fact that when an electric current is passed through solutions of the two salts, the ion containing the silver moves in the first case toward the cathode, and in the second toward the anode.[1]

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[1] The details of an experiment to illustrate this may be found in *Jour. Am. Chem. Soc.*, **22**, p. 732.

All of the elements which are capable of forming chemical compounds, that is, all except those of the argon group, can exist in some sort of ionic condition. Many yield simple ions, with one or more electrical charges, while others can only form a part of complex ions. For example, carbon and nitrogen cannot form, in any appreciable concentration, ions consisting of single charged atoms, but they can form with great readiness such ions as CO_3^{--}, NH_4^+, NO_2^-, and NO_3^-.

A list of the ions of the more common elements which are ordinarily met with in the course of qualitative analysis, together with their most important characteristics, will be found in Chapter V.

34. It should be pointed out here that complex ions, both anions and cations, are formed in great variety, and that their formation frequently increases the apparent difficulty in the application of the Law of Mass Action to specific instances of chemical change. These difficulties lessen, however, with the increase of our knowledge; and when the exact conditions are unknown in a special case, it is frequently possible to draw fairly accurate conclusions from analogies.

35. **Acids.** — All acid solutions possess certain characteristic properties: (1) They turn blue litmus red; (2) they taste sour; (3) they dissolve certain metals with an evolution of hydrogen gas; (4) they neutralize bases; (5) they conduct electricity. All of these properties of solutions of acids are those of one common component, the hydrogen ion, and an acid may be defined as a substance which, in aqueous solution, yields hydrogen ions.

It is well known that acids vary in strength, that is, some yield solutions which are more intensely sour than others, or react more vigorously with such a metal as zinc or magnesium; and a study of the solutions of the various acids has shown that these variations in strength are due to variations in dissociation. The strongest (most active) acids are those which are most dissociated, that is, those which yield the largest relative number of H^+-ions; and, since it has already been stated that the electrical conductivity is also dependent upon the degree of dissociation, it is evident that the *strength* of an acid may be conveniently determined by measuring its conductivity.

36. This may be approximately accomplished with the aid of an apparatus designed by Dr. W. R. Whitney and illustrated in the accompanying figure.[1] In the four vertical tubes are to be placed four acids of different

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[1] For a full description of the details of this experiment see *Jour. Am. Chem. Soc.*, **22**, p. 736.

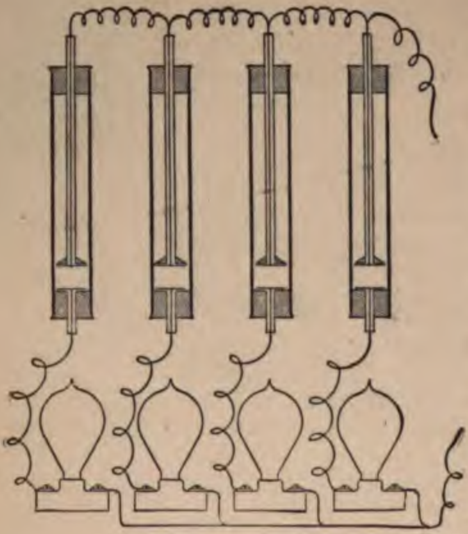

FIGURE 4

degrees of ionization. In each tube are two electrodes; the upper movable, the lower rigid; and in series with each tube is an ordinary incandescent lamp. Connections are made with a lighting circuit (alternating current, 112-volt is best), so that a current may pass through each tube, the magnitude of the current being judged by the brilliancy with which the lamp below that tube glows. If $\frac{1}{30}$ normal solutions of hydrochloric acid, sulphuric acid, chloracetic acid, and acetic acid are placed in the four tubes, and the electrodes are all placed at the same distance apart, the lamp in series with the hydrochloric acid glows brilliantly, that with sulphuric acid a little less brilliantly, that with chloracetic acid much less brilliantly, while that with acetic acid barely glows. If now the upper electrodes are adjusted so that all the lamps glow with equal brightness, it will be found that the distances between the two electrodes bear approximately the ratios 100 : 85 : 15 : 1; that is, the relations of these four acids, with respect to conductivity, degree of dissociation, and strength, are approximately those indicated by these figures.

37. **Bases.** — All basic solutions have the following characteristic properties: (1) They turn red litmus blue; (2) they taste alkaline; (3) they cause a slippery feeling between the fingers; (4) they neutralize acids; (5) they conduct electricity. These are all properties of one common component, the OH^-- or hydroxyl-ion. The strength of a base depends upon the extent to which it is dissociated; that is, upon the relative number of OH^--ions which it yields.

With the same apparatus used above, the relative strength of potassium hydroxide, sodium hydroxide, and ammonium hydroxide may be shown to be approximately 100 : 100 : 1.

38. **Salts.** — If separate solutions of an acid and a base are mixed together there is an immediate reaction, and if the amounts are properly chosen the resulting solution is exactly neutral; that is, it shows none of the characteristic properties of the H^+- or the OH^--ions. The explanation of this becomes clear from an inspection of a reaction represent-

ing such a process of neutralization, $Na^+, OH^- + H^+, Cl^- = HOH + Na^+, Cl^-$, which shows that the principal and important change in the constituents of the solution has resulted in the combination of the H^+- and OH^--ions to form water. As water is practically undissociated, these ions are no longer in a condition to impart their characteristics to the solution. The remaining constituents of the solution are Na^+- and Cl^--ions, and if this solution is evaporated the dissociation of the NaCl gradually lessens as the solution becomes more concentrated, and finally the solid salt separates exactly as was described in the case of the potassium nitrate, on page 27.

A salt is thus a product of the neutralization of an acid and a base, and is formed from the negative ion of the former and the positive ion of the latter. As has already been stated, salts in solution (with very few exceptions) are highly ionized.

If, after showing the relative degree of ionization of the four acids as above described, the upper electrodes are removed, and after adding a drop of litmus, a solution of potassium hydroxide is added drop by drop to each tube until the color barely changes to blue, it will be found, on reinserting the upper electrodes to points one-third of the distance from the bottom of each tube, that all the lamps glow brilliantly and with approximately the same intensity. This shows that the four salts produced by the neutralizations, namely, potassium chloride, potassium sulphate, potassium chloracetate, and potassium acetate, are all ionized to approximately the same extent, regardless of the acid from which they are formed.

39. **Neutralization.** — The essential reaction in the neutralization of an acid and a base is the mutual disappearance of H^+- and OH^--ions. Where both acid and base are highly ionized and the resulting salt is soluble, this is, as already stated, practically the only reaction. The truth of this statement is indicated by the fact that the heat evolved by the neutralization of equivalent quantities of the following strong acids and bases is in all cases the same.[1]

	HCl	HNO_3
NaOH	13,700	13,700
KOH	13,700	13,800

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[1] A calorie is the amount of heat which is sufficient to raise the temperature of 1 gram of water through 1° C. The figures given in the table are the number of calories which are produced by the neutralization of molecular amounts of the various acids and bases.

The heat of the reaction $H^+ + OH^- = H_2O$ is, therefore, 13,700 calories.

As would be expected, the mixing of neutral salt solutions, as potassium nitrate and sodium chloride, where the ionic changes are exceedingly small, produces no appreciable heat effect.

40. When, however, either the acid or base is weak we find that the heat of neutralization is quite different: —

	HCl	HNO_3	$H(C_2H_3O_2)$	H_2S
$NaOH$	. .	. .	13,300	3,800
KOH	. .	. .	13,300	3,800
NH_4OH	12,400	12,500	12,000	3,100

From what has been said above it is evident that the lessening of the amount of heat which is evolved in these cases must be due to some ionic changes within the solution which themselves consume energy. The nature of these changes can best be learned from a study of a typical case, that of the neutralization of acetic acid and ammonium hydroxide.

The dissociation of both of these electrolytes in moderately dilute solutions does not exceed 1 per cent. The conditions of equilibrium within the separate solutions are represented by the expressions: —

$$\frac{\textit{Conc'n}\ H^+ \times \textit{Conc'n}\ Ac^-}{\textit{Conc'n}\ HAc} = \textit{Constant};$$

$$\frac{\textit{Conc'n}\ NH_4^+ \times \textit{Conc'n}\ OH^-}{\textit{Conc'n}\ NH_4OH} = \textit{Constant}.$$

(The values of the two constants are not, of course, the same. The first is found to be 0.000018; the second, 0.000023.)

If now such quantities of the two solutions are mixed as will exactly neutralize each other, a series of changes occurs. At first the H^+- and OH^--ions unite to form undissociated water exactly as in the case of strong electrolytes, and it requires but a moment's reflection to see that this alters the concentration of these ions within the solution, and that, in order that the equilibrium condition may be maintained, more H^+- and OH^--ions must be furnished; that is, that the undissociated HAc- and NH_4OH-molecules must dissociate: —

$$HAc \rightleftharpoons H^+ + Ac^-;$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-.$$

But the H^+- and OH^--ions thus formed also combine, and this procedure is repeated with great velocity until the solution is neutral, and complete equilibrium between all of the components is established; that is, until all of the HAc- and NH_4OH- molecules have been dissociated. At this point the solution will contain only NH_4^+- and Ac^--ions, H_2O, and a very small quantity of undissociated NH_4Ac. It is, then, the energy consumed in the dissociation of the molecules, as indicated in the reactions above, which has lessened the total heat evolved on neutralization as compared with the neutralization of two strong electrolytes, which are almost completely dissociated before they are brought into contact.

The neutral solution of the salt ammonium acetate, since it contains a far greater number of ions than either the base or acid from which it is formed, will also be a far better conductor of electricity.

The Action of a Strong Acid upon the Salt of a Weak Acid

41. It has already been shown, on page 27, that when an insoluble substance can result from a combination of ions within a solution, the reaction continues until one or both of the reacting substances is exhausted; and it has also been demonstrated in the preceding paragraphs that the same conditions hold when H^+- and OH^--ions unite to form water. In both instances the product is an undissociated body.

On the other hand, it has been shown (page 26) that, if the possible products from the interaction of the ions are all substances which are largely ionized, no evidence of chemical change is manifest. Between these two extremes there are many cases in which the product is ionized, but only to a moderate extent, and in such instances a reaction will occur, but it will only partially complete itself. An example is found in the action of a strong acid, as hydrochloric acid, upon the salt of a weak acid, as sodium acetate. If these substances are brought together the odor of undissociated acetic acid (that of vinegar) is at once noticeable. This is occasioned by the union of the H^+-ions from the ionized hydrochloric acid with the Ac^--ions of ionized sodium acetate to form the acetic acid, which (see Appendix) is relatively little dissociated. The reaction is essentially $H^+, Cl^- + Na^+, Ac^- \longrightarrow (HAc) + Na^+, Cl^-$, and the major portion of the weak acetic acid will be displaced from its salt. Since, however, a portion of the acetic acid is dissociated, whereby H^+- and Ac^--ions would result, it is evident that the reaction cannot continue quite to completion.

Thus, any strong acid will displace from a neutral salt of a weak acid the major part of that weak acid in its undissociated form.

42. The Effect of the Formation of Volatile Products.—A third case remains to be discussed, namely, that in which one of the products of the interaction of the ions is relatively volatile.

Even a weaker acid may displace a slight amount of a stronger acid from its neutral salt, as, for instance, when sulphuric acid acts upon sodium chloride a certain amount of undissociated hydrogen chloride is formed.

If, as is true in this case, the slight amount of the new substance formed is volatile, its escape, by reducing its concentration, renders the formation of fresh quantities possible, and under the proper conditions the complete displacement of the stronger acid may be effected by means of the weaker one. Use is made of this fact in the commercial manufacture of hydrochloric acid, in which common salt and concentrated sulphuric acid when heated together react to form sodium sulphate and gaseous hydrogen chloride, the latter of which, when conducted away and dissolved in water, forms the common hydrochloric acid of commerce. This is explained in detail as follows: At a high temperature sodium chloride dissolves to some extent in concentrated sulphuric acid, forming Na^+- and Cl^--ions; concentrated sulphuric acid is also somewhat dissociated, with the formation of a small quantity of H^+-ions. According to the principle of Mass Action a certain proportion of the H^+-ions and Cl^--ions must, under these conditions, unite to form undissociated HCl; but, since the amount of the latter which does form is in excess of its solubility in the strong sulphuric acid, it escapes as a gas nearly as fast as it is produced. Since the liquid will not hold in solution sufficient undissociated hydrogen chloride to maintain an equilibrium with its ionization products, the latter must continuously combine, and since their concentration is constantly maintained through the progressive dissociation of sulphuric acid and sodium chloride, the process is only ended when either one or both of these materials is used up. The apparent reaction is:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

It is the volatility of hydrogen chloride which makes its formation possible; for, if it could not escape from the reacting mixture, the presence of a very small amount of it would prevent its further formation, since it is a stronger (*i. e.*, more largely ionized) acid than sulphuric acid.

43. In general, then, a reversible reaction can continue to a complete disappearance of one or both of the reacting substances upon one side of the equation, if one of the products formed upon the other side is removed from the sphere of action as fast as it is produced. This occurs if this product is insoluble, and either falls as a precipitate or escapes as a gas. In addition, as has already been explained under neutralization of acids and bases, reactions may continue to the complete disappearance of the reacting bodies, if one or more of the products are practically undissociated (as is the case with water), even when these products do not escape from the solution. This is one of the most important consequences of the Mass Action Law.

44. **The Solubility of Carbonates in Acids.** — Most carbonates, except those of the alkali metals, are so little soluble in water that they are generally spoken of as insoluble compounds. Thus, if solutions of sodium carbonate and calcium chloride are poured together, a precipitate forms, according to the reaction: —

$$Ca^{++}, Cl^-, Cl^-, + Na^+, Na^+, CO_3^{--} = 2Na^+, 2Cl^- + \mathbf{CaCO_3}.$$

Calcium carbonate is, however, soluble in acids with an evolution of carbon dioxide gas, as was noted under the discussion of acids as one of the characteristic effects of hydrogen ions. It is necessary, in order to explain why the presence of hydrogen ions should cause an otherwise insoluble substance to dissolve, to assume that calcium carbonate is not absolutely insoluble in water, but that water in contact with it dissolves a very small amount, even although this amount may be so exceedingly small that a solution saturated with it will leave no perceptible residue after evaporation. This very small amount which is dissolved consists of Ca^{++}- and CO_3^{--}-ions. Carbonic acid, which is a very weak acid, dissociates primarily into hydrogen ions and complex negative ions, $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, the latter of which dissociates further, but even to still less an extent, into more hydrogen ions and carbonate ions, $HCO_3^- \rightleftharpoons H^+ + CO_3^-$. Although the solubility product for Ca^{++}- and CO_3^{--}-ions is so extremely small, nevertheless that for Ca^{++}-ions and the more complex HCO_3^--ions is large; that is to say, calcium acid carbonate, $Ca(HCO_3)_2$, is a very soluble salt, as well as one which is to a high degree ionized.

When powdered calcium carbonate is suspended in water, it dissolves until the solubility product of Ca^{++}-ions and CO_3^{--}-ions is reached. If any acid, such as hydrochloric acid, is then added, the CO_3-ions cannot longer remain in even their former small concentration in presence of the H^+-ions of the acid; but the major part of them combine to form HCO_3^--ions, and these again combine with more H^+-ions to form the H_2CO_3-molecules. But by this action the product of the concentrations of Ca^{++}- and CO_3^{--}-ions is diminished below the solubility product, so that more calcium carbonate is able to dissolve. This process is a continuous one so long as there remain H^+-ions in the solution and undissolved calcium carbonate; for, long before enough carbonic acid can have formed in solution to cause the process to reverse, it has itself decomposed into water and carbon dioxide, $H_2CO_3 \longrightarrow H_2O + CO_2$, the latter escaping as a gas.

The completeness with which this reaction takes place is due to two causes: first, to the slight tendency of the HCO_3^--ions, as well as of H_2CO_3-molecules, to dissociate; and second, to the insolubility of carbon dioxide in water.

45. The Precipitation of the Metallic Sulphides.—When a stream of hydrogen sulphide gas is passed into an acid solution of copper chloride, a black precipitate of copper sulphide is formed. Hydrogen sulphide is somewhat soluble in water, forming in it a very weak acid,[1] $H_2S \rightleftharpoons H^+ + H^+ + S^{--}$. In a solution containing also hydrochloric acid, the concentration of S^{--}-ions will be very much diminished below that in a solution containing no strong acid; for, in the former case, the concentration of the H^+-ions is many times increased, and the dissociation of the hydrogen sulphide, and consequently the concentration of the S^{--}-ions, must be correspondingly greatly decreased in accordance with the Law of Mass Action. Therefore the solubility product of copper sulphide must be exceedingly small, if even in a *strongly acid* solution of hydrogen sulphide there are sufficient S^{--}-ions to form a precipitate with Cu^{++}-ions.

Zinc behaves differently from copper in that it is only partially thrown down in the form of sulphide when hydrogen sulphide is passed into a neutral solution of zinc chloride, or one faintly acid with hydrochloric acid, while precipitation is entirely prevented by any considerable quantity of hydrochloric acid. An explanation of this is found in the fact that the solubility product of zinc sulphide, although small, is still very many times greater than that of copper sulphide. As long as the solution of the zinc salt is neutral or only feebly acid, the hydrogen sulphide is sufficiently dissociated to yield S^{--}-ions in such quantity that the solubility product of the zinc sulphide is exceeded, and precipitation ensues. But as soon as the concentration of the hydrochloric acid is considerable, the total concentration of the H^+-ions is so far increased that that of the S^{--}-ions is decreased to a point below that at which, multiplied by the concentration of the Zn^{++}-ions, it gives a quantity equal to the solubility product of zinc sulphide, therefore precipitation can no longer occur.

That the solubility product of ferrous sulphide, again, is greater than that of zinc sulphide or copper sulphide is indicated by its failure to precipitate when hydrogen sulphide is passed into even a neutral solution of ferrous chloride. If, on the other hand, a solution of ammonium sulphide is added to such a solution the iron is at once completely precipitated as ferrous sulphide, because, ammonium sulphide being a salt, it is largely ionized in solution, and, since it is very soluble in water, it yields so many S^{--}-ions that, even with a small amount of Fe^{++}-ions, the solubility product of the ferrous sulphide is readily exceeded. For the same reason zinc would also be completely precipitated by this reagent from a solution of a zinc salt. The ionic changes in the case of the iron salt are as follows: —

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[1] The intermediate ion, HS^-, which dissociates further into H^+- and S^{--}-ions, is also present here, but in this explanation simplicity is gained, and no serious error is made, by leaving it out of consideration.

$$NH_4^+, NH_4^+, S^{--} + Fe^{++}, Cl^-, Cl^- = \mathbf{FeS} + 2NH_4^+, 2Cl^-.$$

It should be remembered that the solubility product of ferrous sulphide, although larger than that of the zinc sulphide, is still small, otherwise no precipitation could occur.

THE ACTION OF A STRONG BASE UPON THE SALT OF A WEAK BASE

46. If sodium hydroxide is added to a solution of ammonium chloride the odor of ammonia becomes apparent. The OH^--ions of the strong base, sodium hydroxide, unite with NH_4^+-ions of the salt to form the weakly dissociated base, ammonium hydroxide, $Na^+, OH^- + NH_4^+, Cl^- = (NH_4OH) + Na^+, Cl^-$. Ammonium hydroxide dissociates also non-electrolytically to some extent into water and ammonia, $NH_4OH \rightleftharpoons H_2O + NH_3$, and the small amount of the latter which escapes as a gas indicates by its odor the existence of ammonium hydroxide in the solution.

The action of a strong base upon a salt of a weak base results always, as in the above instance, in the formation of a greater or less amount of the undissociated weak base. It should be noted that this is comparable with the action of a strong acid upon the salt of a weak acid.

EFFECT UPON THE PROPERTIES OF WEAK ACIDS OR BASES OF NEUTRAL SALTS WITH A COMMON ION

47. The acid or basic character of weak acids or bases is very greatly reduced by the presence of any highly ionized neutral salt with a common anion or cation. This will be clear from the following illustration: —

In a solution of acetic acid a comparatively small number of HAc-molecules dissociate into an equal number of H^+- and Ac^--ions, until a state of equilibrium is reached, when

$$\frac{\textit{Conc'n}\ H^+ \times \textit{Conc'n}\ Ac^-}{\textit{Conc'n}\ HAc} = \textit{Constant}.$$

In a molal solution of pure acetic acid the H^+-ions and Ac^--ions have been proved to be present in a concentration 0.0042 molal, *i. e.*,

$$\frac{.0042 \times .0042}{.9958} = .000018.$$

But in a solution which is molal with regard to sodium acetate as well as acetic acid (since sodium acetate at that concentration is known to be 50 per cent. dissociated), the concentration of Ac^--ions will be 0.50 molal. The concentration of undissociated acetic acid molecules is so nearly that of the total amount present (1.0 molal) that it may practically be placed at that figure. Calling x the concentration of H^+-ions, the formula becomes:—

$$\frac{x \times 0.50}{1.0} = 0.000018, \quad \text{or} \quad x = 0.00004.$$

Therefore the concentration of the H^+-ions has been reduced to $\frac{1}{100}$ of its previous value by the presence of an equivalent quantity of neutral sodium acetate, or, to put it in another form, the strength or efficiency of the acetic acid has been lessened, since, as has already been stated (page 33), the strength of an acid depends upon the concentration of the H^+-ions which it yields.

The basic character of ammonium hydroxide is so diminished by the presence of ammonium chloride that, as will be mentioned in Chapter V, ammonia fails, in the presence of the latter reagent, to give the usual precipitates of the hydroxides of cobalt, magnesium, etc.

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HYDROLYSIS

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48. When perfectly pure potassium cyanide is dissolved in water the solution acquires an alkaline reaction; that is, it exhibits the characteristic reactions for OH^--ions, and turns red litmus blue. When pure ferric chloride is dissolved in water the solution acquires an acid reaction; that is, it shows the reactions of H^+-ions, and turns blue litmus red.

In order to explain these phenomena it is necessary to take into account certain properties of the pure solvent water which have been disregarded in the preceding discussions, namely, the presence in the water of a very small quantity of H^+- and OH^--ions. It is quite true that the extent of this dissociation is so slight that it may ordinarily be neglected — that it does not appreciably affect, for example, the completeness of the neutralization reactions of strong acids and bases. On the other hand, it does attain some significance when it becomes necessary to consider bodies which, while exhibiting greater dissociation than the water, are not far removed from it in this particular.[1] In such cases the phenomena known as *hydrolysis* makes itself evident; that is, the dissociated water takes a part in the chemical action. This will be best understood by considering in detail the hydrolysis of the two salts mentioned above.

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[1] In 1 liter of pure water there is present but $\frac{1}{10000000}$ of a mol of H^+- or OH^--ions. The extent to which some of the most important electrolytes are dissociated is given in the Appendix.

These two substances, in conformity with the general rule regarding neutral salts, are highly ionized: —

$$\mathrm{KCN} \longrightarrow \mathrm{K}^{+} + \mathrm{Cn}^{-};$$
$$\mathrm{FeCl}_3 \longrightarrow \mathrm{Fe}^{+++} + \mathrm{Cl}^{-} + \mathrm{Cl}^{-} + \mathrm{Cl}^{-}.$$

Hydrocyanic acid, however, which is the acid from which potassium cyanide is formed, is a substance which is dissociated but little more than water, and although the amount of H^+- and OH^--ions into which pure water is dissociated is so slight, yet the degree of dissociation of hydrocyanic acid is also so small that not even the H^+-ions normally present in water can remain as such in the presence of the CN^--ions of potassium cyanide. A formation of undissociated hydrogen cyanide results, $H^+ + CN^- \longrightarrow HCN$. Since the equilibrium between water and its ions is thereby disturbed, more water must dissociate to furnish a fresh supply of H^+-ions, $H_2O \longrightarrow H^+ + OH^-$. The H^+-ions thus formed being once more in excess of the number which can remain in equilibrium with the CN^--ions and the HCN-molecules already formed, the process continues until a point of equilibrium is reached when the amount of undissociated hydrogen cyanide no longer increases.

Since the progressive dissociation of water must have yielded OH^--ions equal in number to the H^+-ions, and since those ions have but a very slight tendency to combine with K^+-ions to form undissociated KOH, they must have accumulated in the solution, thereby giving it its basic character.

The hydrolysis of potassium cyanide thus consists of a partial reaction of this salt with water, with a formation of equivalent amounts of free hydrocyanic acid, undissociated (and therefore inactive), and of free potassium hydroxide (dissociated and active), the latter of which gives to the solution its basic properties. That hydrolysis is exactly the reverse of neutralization is shown by this equation: —

$$\mathrm{HCN} + \mathrm{K}^{+}, \mathrm{OH}^{-} \rightleftharpoons \mathrm{HOH} + \mathrm{K}^{+}, \mathrm{CN}^{-}.$$

49. The hydrolysis of ferric chloride, on the other hand, can only result in the formation of hydrochloric acid and ferric hydroxide, the latter a body which is about as little dissociated as hydrogen cyanide. Hence in a solution of ferric chloride the OH^--ions, which are normally present in pure water, cannot exist in the presence of the Fe^{+++}-ions, and a formation of undissociated ferric hydroxide is the result, $Fe^{+++} + 3OH^- \longrightarrow Fe(OH)_3$. This removal of OH^--ions permits more water to dissociate, and this process continues until an appreciable amount of undissociated ferric hydroxide and of ionized hydrochloric acid has been formed, the H^+-ions of the latter imparting to the solution its acid reaction. The hydrolysis of ferric chloride is thus exactly the reverse of the neutralization of ferric hydroxide and hydrochloric acid:—

$$FeO_3H_3 + 3H^+, 3Cl^- \rightleftharpoons Fe^{+++}, 3Cl^- + 3H_2O.$$

50. It is to be noted that in the case of potassium cyanide a weak acid is combined with a strong base, while in ferric chloride the reverse is true. Salts formed from strong acids and strong bases are not hydrolyzed and give a perfectly neutral reaction with litmus. The reason for this will be evident if it is recalled that when sodium chloride, for example, is dissolved it dissociates into Na^+- and Cl^--ions, neither of which have more than a very slight tendency to combine with OH^-- or H^+-ions, respectively, and that therefore the amounts of undissociated NaOH and HCl which are formed are entirely too small to disturb the equilibrium which exists between water and its ions.

On the other hand, the hydrolysis of a salt which is formed from an acid and a base both of which are weak may be so complete that it will not be possible for the salt to exist in solution. For example, when ammonium sulphide is added to a solution of aluminum chloride, instead of the formation of aluminum sulphide within the solution, there will appear its hydrolyzation products, aluminum hydroxide and hydrogen sulphide. Since both of these will be formed in excess of their solubility, the former will fall as a precipitate and the latter will escape as a gas:—

$$\begin{aligned}2Al^{+++}, 6Cl^- + 6NH_4^+, 3S^{--} + 6H^+, 6(OH)^- &= \\ 6NH_4^+, 6Cl^- + \mathbf{2Al(OH)_3} + 3(H_2S).&\end{aligned}$$

CHAPTER III

ELECTROLYTIC SOLUTION PRESSURE

51. It is well known that where strips of zinc, iron nails, or other fragments of iron are immersed in solutions of copper salts, the zinc or the iron at once becomes coated with copper, and a qualitative examination of the solution shows that some of these metals have simultaneously dissolved. This process of interchange will continue until the zinc or iron has entirely dissolved, leaving in its place a spongy mass of metallic copper; or, if the zinc or iron is in excess, the process will continue until all of the copper is removed from the solution. Platinum or silver, on the other hand, if immersed in a solution of the same copper salt causes no visible change. To explain these differences it is necessary to consider in detail the process which has gone on between the zinc and the copper salt.

It is found by quantitative experiments that for every 63.6 grams of copper deposited 65.4 grams of zinc pass into solution. These quantities represent the atomic weights in grams of the two metals. It is, therefore, evident that for every atom of copper deposited from solution an atom of zinc passes into solution; and, with this as a starting point, the behavior of the two metals is easily explained by the ionic theory, as follows: The metallic zinc is made up of electrically neutral zinc atoms; copper sulphate in solution exists essentially in the form of Cu^{++}- and SO_4^{--}-ions; zinc sulphate exists in solution as Zn^{++}- and SO_4^{--}-ions. The real change, then, is, $\mathbf{Zn} + Cu^{++}, SO_4^{--} \longrightarrow \mathbf{Cu} + Zn^{++}, SO_4^{--}$; that is, an electrically neutral zinc atom has become a Zn^{++}-ion by assuming positive charges, while a Cu^{++}-ion has become an electrically neutral copper atom by giving up exactly equivalent positive charges. This expressed as an equation is:—

$$\mathbf{Zn} + Cu^{++} = \mathbf{Cu} + Zn^{++}.$$

In still greater detail this process may be described as follows: The fact that the strip of zinc is electrically neutral implies that whatever charges of positive and negative electricity reside upon it must be equal. As the Zn^{++}-ions separate from it, carrying their positive charges, the strip retains residual negative charges which attract the positively charged Cu^{++}-ions of the solution, which thus have their charges neutralized by the negative charge on the strip of zinc, and deposit as copper atoms. The solution pressure of copper is so small that these atoms do not, like those of zinc, tend to return to the solution as ions.

The metals cannot dissolve in the form of neutral atoms, but must enter the solution as electrically charged ions; and experiment has shown that every metal has a definite tendency to pass from the atomic to the ionic condition, just as the zinc does in the above illustration. This impelling force is known as the *electrolytic solution pressure* for the metal in question, and this quantity is found to be capable of estimation and to be a characteristic property of the metal.

It is evident that the metal zinc in the illustration above cannot, in spite of the great solution tension which it possesses, simply pass into solution as ions with no other accompanying change; for if this did occur, even to a very slight extent, the solution would then be charged with a great surplus of positive electricity, since the ions bear enormous charges. The zinc ions, with their positive charges, would now, not being balanced by negatively charged ions, repel each other with a force far greater than the solution tension of the metal, so that the zinc ions would be forced out of solution again into the original neutral metallic condition.

But if the strip of zinc is placed in a solution containing positive ions of some element with a lesser solution tension (see table on page 47), as, for example, the solution of copper sulphate, there will then be an outlet by which the positive electricity carried into solution by the zinc ions can escape — or, more exactly, by which an equivalent amount of positive electricity may escape — namely, by the giving up of the positive charges of the copper ions at the surface of the zinc, whereby they themselves assume the form of neutral copper atoms, and their positive electricity neutralizes the negative electricity induced on the metal strip as the result of the formation of positive ions.

52. The electrolytic solution pressure may be regarded as a phenomenon of the same general nature as osmotic pressure; in fact, the force of this tension may be expressed in terms of the osmotic pressure of the ions of the respective metals, which will just suffice to counterbalance it. In the table below the metals are arranged in the order of the magnitude of their respective solution pressures, the values of which are expressed in atmospheres so far as they are accurately known.

Electrolytic Solution Pressure of the Metals[1]

Sodium	Na^+	. . .	Lead	Pb^{++}	1.1×10^{-3}
Calcium	Ca^{++}	. . .	Hydrogen . . .	H^+	9.9×10^{-4}
Magnesium . . .	Mg^{++}	1.1×10^{43}	Bismuth	Bi^{+++}	. . .
Aluminum . . .	Al^{+++}	. . .	Antimony		. . .
Manganese . . .	Mn^{++}	. . .	Arsenic		. . .
Zinc	Zn^{++}	9.9×10^{18}	Copper	Cu^{++}	4.8×10^{-20}
Cadmium	Cd^{++}	2.7×10^{6}	Mercury	Hg^+	1.1×10^{-16}
Iron	Fe^{++}	1.2×10^{4}	Silver	Ag^+	2.3×10^{-17}
Cobalt	Co^{++}	1.9	Palladium . . .	Pd^{++}	1.5×10^{-36}
Nickel	Ni^{++}	1.3	Platinum		. . .
Tin	Sn^{++}	. . .	Gold		. . .

The electro-positive character of the metals decreases in the same order as the solution pressure, and, in general, any metal if immersed in the solution of a salt of a metal with a less solution pressure (*i.e.*, one which is less electro-positive) tends to cause the deposition of that metal from solution as the zinc or iron precipitates copper.

Certain apparent exceptions to this principle are referred to below.

53. It will be noted that hydrogen has been included in the table above. This element resembles the metals in possessing a definite solution pressure; and since hydrogen ions are, as we have seen, always present in minute quantities in aqueous solutions and in considerable quantities in acid solutions, the relation of this pressure to those of the various metals becomes of importance.

All metals with a greater solution tension than hydrogen will dissolve in acids with the liberation of hydrogen gas, provided the salts formed are not themselves insoluble. The action of hydrochloric acid upon zinc is a familiar instance, and demands consideration in detail. When a piece of zinc is immersed in the acid its solution pressure at once causes it to send off zinc ions into the solution, and as these ions with their positive charges leave the mass of zinc the latter becomes negatively charged, as described at the top of page 46. The H^+-ions in the acid solution, like the Cu^{++}-ions in a solution of a copper salt, now discharge themselves upon the zinc, become hydrogen atoms, and these combine to form molecules of hydrogen gas, which escape from the solution, $\mathbf{Zn} + 2H^+ = (H_2) + Zn^{++}$. If, on the other hand, the solution pressure of the metal is less than that of hydrogen, as is the case with copper, the hydrogen ions are not discharged, and no apparent action ensues.

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[1] The position of those metals for which no value is given is only approximate. The values which are given represent the tendency to form the particular ion of the metal which is indicated. Those metals which are not followed by the symbol of an ion do not possess, to more than an infinitesimal extent, the power to yield simple positive ions in solution.

It will be noticed that copper is placed above mercury and silver in the series, although it has a smaller solution pressure than either of those metals. This is because the effect of the double positive charge on the Cu^{++}-ion more than counterbalances the greater solution pressure of the mercury or the silver, so that copper is able to replace these metals from their solutions.

54. It happens in some cases in actual practice that the phenomena as above described do not appear to take place according to the theory; that is, that metals with lower solution pressure are not always thrown out of solution by those of higher solution tension. For example, if a piece of perfectly pure zinc is placed in a solution of an acid there is no evolution of hydrogen gas. This may be explained by assuming that a certain number of zinc ions do go into solution, thereby forcing an equal number of hydrogen ions into the condition of uncharged atoms, but that these atoms, instead of forming molecular hydrogen, are absorbed uniformly by the uniform surface of the pure zinc, and thus form a sort of protective layer so that further action is stopped. If now a piece of platinum wire is brought into contact with the piece of zinc beneath the liquid, action immediately commences. Zinc goes into solution as Zn^{++}-ions and hydrogen gas escapes, but only from the surface of the platinum wire and not from the zinc. The platinum has broken the protective coating about the metal, and, being in electrical contact with it, a part of the negative charge induced by the loss of positive ions flows into the wire and attracts the positively charged H^+-ions which are here free to discharge themselves, thus leaving the solution in a condition in which it can receive more positive ions from the zinc.

In ordinary commercial zinc it is to be noted that the surface is covered with minute particles of various impurities which serve the same end as the platinum wire above; that is, furnish points at which the hydrogen gas can form and escape. Commercial zinc, therefore, as is well known, dissolves with ease in acids.

55. Again, it is to be noted that the readiness with which ions of a metal pass into a solution is influenced by the number of ions of that metal already in the solution. Thus there is more tendency for ions of cobalt to leave a rod of cobalt immersed in a solution containing no cobalt ions than if the solution already contained a cobalt salt. Conversely, in an acid solution the tendency of hydrogen ions to pass into the electrically neutral state is greater the higher the concentration of these ions. It is for this reason that metals react more vigorously the stronger the acids with which they are in contact, because the reaction is a result of the combined tendencies of the metal to pass into the ionic form and of the hydrogen ions to pass into the neutral condition. Since pure water contains so exceedingly few hydrogen ions, it is apparent why many metals which possess much higher solution tensions than hydrogen, and accordingly attack acids readily, have no effect upon water.

THE ELECTROLYTIC IONIZATION PRESSURE OF THE NEGATIVE ELEMENTS, OR THE TENDENCY OF THESE ELEMENTS TO PASS INTO THE IONIC CONDITION

56. When chlorine gas is bubbled into a solution of potassium iodide, free iodine is liberated which colors the solution brown, and the chlorine is found to have taken the place of iodine in the compound, forming potassium chloride: $(Cl_2) + 2K^+, 2I^- = 2K^+, 2Cl^- + (I_2)$; or, more simply, $(Cl_2) + 2I^- = 2Cl^- + (I_2)$.

This case differs from that of the replacement of copper by zinc simply in the fact that here the electrically neutral elements are themselves soluble, and that as ions they assume negative instead of positive charges.

Each of the negative elements which can form simple ions is characterized by a certain definite tendency to do so, which is similar to the electrolytic solution tension of the positive elements, and they may also be arranged in a series according to the magnitude of their ionization tensions. Any element in such a series would be more electro-negative than any element standing below it, and would displace the latter from its salts when dissolved in water.

Although, owing to the experimental difficulties involved, exact values have not been obtained, yet the order in which the negative elements stand with respect to their tendency to form ions is shown in the following table[1]:—

Fluorine	F^-
Chlorine	Cl^-
Bromine	Br^-
Oxygen	. .
Iodine	I^-
Sulphur	S^{--}

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[1] Oxygen would naturally first form the ion O^{--}; this ion cannot, however, attain any appreciable concentration, because as fast as it is formed it reacts with other constituents of the solution as follows: $O^{--} + H^+ = OH^-$, or $O^{--} + H_2O = 2OH^-$.

57. It has already been stated, on page 18, that the explanation there given in connection with the electrolysis of potassium sulphate did not take into account all of the factors involved. It has since been shown that water is itself dissociated to a slight extent into H^+- and OH^--ions, and it may now be stated that an exceedingly small fraction of the latter are further dissociated into H^+- and O^{--}-ions. In the light of these facts the full explanation takes the following form: At the cathode the K^+-ions which bring the current through the solution to that electrode might give up their charges,[1] but, since potassium has such an enormously greater solution tension than hydrogen, the few H^+-ions, in the layer of solution immediately surrounding the cathode will give up their charges and go into the neutral condition in preference to the K^+-ions. As fast as the H^+-ions disappear in this manner more water molecules will dissociate in accordance with the Mass Action Law, to furnish a new supply of H^+-ions. This process is continuous, and the OH^--ions, which are also formed by the dissociation of water, remain in the solution and electrically balance the K^+-ions which do not discharge.

At the anode the SO_4^{--}-ions which bring the current to the electrode might discharge, if no negative ions were present which could more easily part with their charges. The O^{--}-ions in the layer surrounding the anode can, however, discharge more readily than the SO_4^{--}-ions, because their tendency after they are discharged to reassume the ionic form is less; therefore it is the O^{--}-ions which do give up their negative charges, and more water molecules dissociate to give fresh O^{--}-ions, while H^+-ions remain in the solution to electrically balance the SO_4^{--}-ions which do not discharge.

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[1] Indeed, this does occur with a very heavy current when a cathode of mercury is used, which dissolves the potassium set free, and thus lessens its tendency to react with the water.

CHAPTER IV

OXIDATION AND REDUCTION

58. When iron rusts in the air, forming iron oxide, there is a direct addition of oxygen, and the process is called oxidation. If the oxide is heated in a stream of hydrogen and its oxygen thereby removed, it is said to be reduced. Instead of oxygen, any electro-negative element, as sulphur or chlorine, can be made to unite with iron to form iron sulphide or iron chloride, and, again, by suitable means iron may be freed from the negative element in these compounds. The meaning of the terms oxidation and reduction has been extended to include cases such as the latter, in which other negative elements than oxygen are added or removed.

59. When iron is dissolved in hydrochloric acid it passes from the electrically neutral metallic condition into the form of electrically charged ions, while hydrogen ions simultaneously release their charges, thereby assuming the form of the neutral element. If the resulting solution is evaporated, solid ferrous chloride is obtained. The iron is evidently in the same condition as if it had been made to combine directly with chlorine gas; that is, it is in the oxidized state. It may be asked, Is, then, the mere fact that it is combined with a negative element a criterion of its oxidation, or is it to be considered as oxidized even when in solution as the ion Fe^{++}? The important change which takes place during the transformation of iron into solid ferrous chloride, when this is accomplished by first dissolving in hydrochloric acid and then evaporating, really occurs when iron atoms acquire positive charges at the expense of hydrogen ions; the mere gradual evaporation of water, so that the Fe^{++}- and Cl^{-}-ions unite more and more as $FeCl_2$-molecules, does not essentially alter any characteristic of ferrous chloride. Therefore the oxidation of iron when it is dissolved must consist in the imparting to it of the positive charges of electricity, and the substance from which it receives these charges, that is, hydrogen, must be correspondingly reduced.

60. But iron can exist in different states of oxidation. If chlorine gas is bubbled into the solution of ferrous chloride, as formed above, until no more is absorbed, and this solution is then evaporated, solid ferric chloride, $FeCl_3$, is obtained. The iron has thus been further oxidized. The reaction in the solution is as follows: $2Fe^{++} + 4Cl^- + (Cl_2) = 2Fe^{+++} + 6Cl^-$. The ferrous ion has acquired one more positive charge, by which it is changed to the ferric ion, possessing properties which are as much at variance with those of ferrous ions as if it were the ion of an entirely different element.

But, since the iron has been oxidized, there must have been some corresponding reduction. Chlorine gas, when it is first dissolved in water, does not dissociate, but forms electrically neutral molecules. The fact that the molecules are electrically neutral implies merely that they possess no excess of either positive or negative electricity. They probably do possess a certain quantity of each, but in exactly equal amounts. At the moment in which chlorine takes part in the reaction noted above each molecule changes into two negative ions, and since two negative charges have thereby appeared the two positive charges by which they were previously held inactive must have also appeared at some point. They have attached themselves to two Fe^{++}-ions, converting them into Fe^{+++}-ions, which are now capable of balancing two additional negative Cl^--ions. In this way the electrically neutral chlorine molecule by changing into chlorine ions has lost positive charges, which is another way of saying that it has undergone reduction. On the other hand, the Fe^{++}-ions have acquired positive charges at the expense of the chlorine and are oxidized.

61. An element, then, as has been shown for iron, can be oxidized (1) by causing atoms of a negative element to combine with it; or (2) by imparting positive charges of electricity to its atoms, converting them into ions; or (3) by imparting additional positive charges to its already existing ions. Ions, however, like the neutral elements, may be oxidized by the addition of atoms of negative elements as well as by the imparting of positive charges, as illustrated by the change of SO_3^{--} to SO_4^{--}, or of AsS_3^{---} to AsS_4^{---}. For example, when a solution of sulphurous acid is exposed to the air, it slowly absorbs oxygen, and sulphuric acid is formed, $2H_2SO_3 + O_2 = 2H_2SO_4$, or

$SO_3{}^{--} + O = SO_4{}^{--}$. When a solution of sodium sulpharsenite is treated with sulphur (dissolved in Na_2S) it is oxidized to sodium sulpharsenate, $Na_3AsS_3 + S = Na_3AsS_4$, or $AsS_3{}^{---} + S = AsS_4{}^{---}$.

The oxidation of any body may, then, consist in the addition of atoms of a negative element to its molecules, atoms, or ions, or the withdrawal of the atoms of a positive element; or it may consist in the addition of positive charges of electricity, or the withdrawal of negative charges.

Reduction is the reverse of this, namely, the addition of the atoms of positive elements or of negative electrical charges, or the withdrawal of the atoms of negative elements, or of positive electrical charges.

The changes in the state of oxidation which the elements may undergo are very characteristic of them, and, like the formation of precipitates by the uniting of oppositely charged ions, may be used extensively in the identification of the various elements in qualitative analysis.

In Chapter V, under the reactions of the ions, will be found the more important oxidation changes which the common ions may undergo, but in the next few paragraphs some typical instances will be discussed in more detail.

62. Tin can exist in its compounds in two different states of oxidation which correspond to the oxides SnO and SnO_2, in which the valence of tin is II and IV, respectively. Corresponding to these variations in valence, tin can form Sn^{++}- and Sn^{++++}-ions, which exist, respectively, in solutions of stannous and stannic chloride, $SnCl_2$ and $SnCl_4$.

Mercury in its compounds can likewise exist in two different states of oxidation, which correspond to the oxides Hg_2O and HgO, in which the valence is I and II, respectively. Mercury likewise forms two ions, Hg^+ and Hg^{++}, which are found in solutions of mercurous and mercuric nitrate, $HgNO_3$ and $Hg(NO_3)_2$.

The stannous ion has a strong tendency to take on more positive charges of electricity, thereby passing into the form of the stannic ion, while the mercuric ion can readily give up one positive charge, thereby becoming a mercurous ion; and the latter, again, can give up its charge and become a neutral mercury atom. When, therefore, a solution of mercuric chloride is treated with stannous chloride one of two reactions will take place, according to the amount of the latter reagent which is used; the Hg^{++}-ions will be reduced either to Hg^{+}-ions, which unite with Cl^{-}-ions to give a white precipitate of mercurous chloride, or they will be completely reduced to metallic mercury, which appears in the form of a black precipitate: —

$$2\overset{II}{Hg}Cl_2 + \overset{II}{Sn}Cl_2 = 2\mathbf{\overset{I}{Hg}Cl} + \overset{IV}{Sn}Cl_4 ;$$
$$\overset{II}{Hg}Cl_2 + \overset{II}{Sn}Cl_2 = \mathbf{\overset{0}{Hg}} + \overset{IV}{Sn}Cl_4 .$$

The valence of any element when in the uncombined state is to be regarded as zero, as is indicated for the metallic mercury appearing in the last reaction. The ionic changes which occur in these reactions are: —

$$2Hg^{++} + Sn^{++} = 2Hg^{+} + Sn^{++++} ;$$
$$Hg^{++} + Sn^{++} = \mathbf{Hg} + Sn^{++++} .$$

63. Sulphur can exist both uncombined and in three different states of oxidation, corresponding to the compounds H_2S, SO_2, and SO_3, in which it has respectively a negative valence of II and a positive valence of IV and VI; that is, it has a valence of II as an element which is negative toward hydrogen, and a valence of IV or VI as an element which is positive with respect to oxygen. Corresponding to these valences, it forms the ions S^{-} , SO_3^{--}, and SO_4^{--}, which occur in solutions of sodium sulphide, sodium sulphite, and sodium sulphate, respectively.

As has been seen, the solution pressure of sulphur, by virtue of which it would pass into solution as negative ions, is very small. Therefore its ions can readily be forced out of solution to produce the free element, and any oxidizing agent, as, for instance, chlorine water or potassium permanganate, will cause a precipitation of free sulphur if it is added to a solution of hydrogen sulphide: —

$$H_2S + Cl_2 = 2HCl + \mathbf{S} ;$$
$$5H_2S + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5\mathbf{S},$$

or

$$S^{--} + Cl_2 = 2Cl^{-} + \mathbf{S} ;$$
$$10H^{+} + 5S^{--} + 5O = 5H_2O + 5\mathbf{S}.$$

The free sulphur so formed is not easily oxidized further, although this can be brought about, as, for example, by boiling with concentrated nitric acid, whereby sulphuric acid is produced. Sulphur can most readily be oxidized by allowing it to burn in the oxygen of the air, forming sulphur dioxide, and this, when dissolved in water, gives sulphurous acid, which yields SO_3^{--}-ions, $SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{--}$. Sulphur in this state of oxidation possesses a valence of IV. This fact is readily seen from the compound SO_2, but in the ion SO_3^{--} it is not at first glance so apparent. Three O-atoms possess the combined negative valence of VI; two of these may, however, be considered to be exerted in holding the negative charges of the ion, so that four only remain to bind the four positive valences upon the S-atom. Tetravalent sulphur has, however, quite a strong tendency to pass into some other state of oxidation, so that sulphurous acid, if treated with any oxidizing agent, is converted into sulphuric acid, $H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI$, or $SO_3^{--} + O^{--} + (I_2) = SO_4^{--} + 2I^-$.

64. Chromium most frequently occurs in its compounds in one of two states of oxidation, represented by the oxides CrO_3 and Cr_2O_3, and in these compounds its valence is either VI or III. The compounds derived from CrO_3 are yellow or red, those from Cr_2O_3 are green or blue; and whenever a change in the state of oxidation occurs it is accompanied by a change in color. Potassium bichromate, $K_2Cr_2O_7$, is typical of the compounds in which chromium has a valence of VI. Its ions, when it is dissolved, are $2K^+$ and $Cr_2O_7^{--}$. In the latter the combined negative valences of the oxygen atoms are fourteen. Two of these are filled by the negative charges on the ion, thus leaving twelve to hold twelve positive valences of the two hexavalent Cr-atoms. When potassium bichromate is subjected to the action of a reducing agent, as, for example, when nascent hydrogen is produced in, or when hydrogen sulphide is passed into, a solution of it which contains also a free acid, a change of color takes place from yellow to green, which indicates a reduction: —

$$K_2\overset{\text{VI}}{Cr_2}O_7 + 8HCl + 6H = 2KCl + 2\overset{\text{III}}{Cr}Cl_3 + 7H_2O,$$

or

$$Cr_2O_7^{--} + 8H^+ + 6(H) = 2Cr^{+++} + 7H_2O.$$

By this reaction the ion $Cr_2O_7^{--}$, on conversion into two Cr^{+++}-ions, has lost fourteen equivalents in the seven atoms of negative oxygen, but has lost two negative charges and gained six positive charges of electricity — an algebraic total of eight charges, so that the total change has been what may be called a loss of six oxidation equivalents. These six equivalents of oxygen have been transferred to the six neutral atoms of hydrogen, whereby they are converted into water molecules. Thus in this as in all reactions there is, for every equivalent of reduction, a corresponding amount of oxidation. It is to be noted that the H^+-ions which appear on the left side of the equation, although they disappear as such, do not suffer either oxidation or reduction, for they have merely become part of H_2O-molecules.

65. Among the various possible oxides of manganese are MnO and Mn_2O_7, in which it exhibits the valences of II and of VII. The compounds of the former are colorless, and of the latter are a very intense reddish violet. When dissolved in an acid the oxide MnO yields the ion Mn^{++}, in which the metal has the same valence, viz., II: —

$$MnO + 2H^+ = Mn^{++} + H_2O.$$

A characteristic compound derived from the oxide Mn_2O_7 is potassium permanganate, $KMnO_4$, which when dissolved in water yields ions as follows: $KMnO_4 \rightleftharpoons K^+ + MnO_4^-$. In the ion MnO_4^- the metal possesses the same valence as in the oxide from which it is derived; for of the eight negative valences of the four oxygen atoms of the ion, one is bound by the negative charge, leaving seven to engage the seven positive valences of the manganese. If an acid solution of potassium permanganate is reduced by means of nascent hydrogen a disappearance of the deep red color takes place: —

$$2KMnO_4 + 10H + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O,$$

or

$$MnO_4^- + 5(H) + 3H^+ = Mn^{++} + 4H_2O.$$

In this case it is seen that the MnO_4^--ion is reduced by five equivalents on conversion into Mn^{++}, while five neutral H-atoms have been correspondingly oxidized with the formation of water. Although the H^+-ions have also combined with oxygen to form undissociated H_2O, yet they have thereby suffered no change in their state of oxidation.

CHAPTER V

THE MORE COMMON IONS AND THEIR CHARACTERISTICS

In order to assist the reader in the specific application of the principles laid down in the foregoing pages to the chemical processes involved in an ordinary course of qualitative analysis or of inorganic preparations, there is given in this chapter a list of the most important ions which are formed from the elements of common occurrence, together with equations showing their important reactions with other ions and their behavior toward oxidizing or reducing agents. In most of the equations only those bodies are included which *actually enter into reaction*, and the reader must constantly keep in mind, when interpreting these equations, the fact that the electrical charges upon one ion, or set of ions, must at all times be balanced by those on some other ions of opposite electrical charge, and that these other ions do not always appear in the equations. For example, the ionic reaction

$$Ag^+ + Cl^- = \mathbf{AgCl}$$

expresses only the important ionic change upon which reactions such as the following depend: —

$$Ag_2SO_4(\text{soln.}) + 2KCl(\text{soln.}) = 2\mathbf{AgCl}(\text{ppt.}) + K_2SO_4(\text{soln.})$$
$$AgNO_3(\text{soln.}) + HCl(\text{soln.}) = \mathbf{AgCl}(\text{ppt.}) + KNO_3(\text{soln.})$$

It is evident, then, that this chapter can only be successfully studied in connection with the reading of the descriptive chemistry of the elements involved, and with a knowledge of the complete reactions of which these are a simplified form.

No attempt has been made to include in this chapter detailed descriptions of the qualitative tests for ions, but rather to explain from the standpoint of the Electrolytic Dissociation Theory certain of the tests which are described in any of the standard manuals of qualitative analysis.

THE IONS OF THE METALS

Silver

(1) Ag^+ colorless, exists in acid or neutral soln.

with Cl^-: a white, curdy ppt., AgCl, which turns black on exposure to the light. It is sol. in NH_4OH and KCN, due to the formation of complex ions (2) and (3).

with S^{--}: a black ppt., Ag_2S, insol. in acids or bases.

with OH^-: the fairly strong base AgOH is formed, which, however, is but slightly sol. It separates from soln. in the form of the brown ppt. Ag_2O. This ppt. will dissolve in pure water to such an extent that its soln. will color litmus blue.

(2) $Ag(NH_3)_2^+$ stable in an ammoniacal soln. It does not form a ppt. with Cl^- nor with Br^-, if a large excess of NH_4OH is present; but with I^-, a yellow ppt., AgI, because the complex ion is still dissociated sufficiently to give a concentration of Ag^+-ions which with I^--ions will exceed the solubility product of AgI. The solubility product decreases for the three salts in the order AgCl, AgBr, AgI. The complex ion is destroyed by acids: — $Ag(NH_3)_2^+ + 2H^+ = Ag^+ + 2NH_4^+$.

with S^{--}: a ppt. of Ag_2S.

(3) $Ag(CN)_2^-$ a very stable ion in neutral or alkaline soln.

with Cl^-, Br^-, I^-: no ppt.

with S^{--}: black ppt., because the complex ion gives sufficient Ag^+-ions to exceed the solubility product of Ag_2S.

with acids: the complex ion is destroyed: —

$$Ag(CN)_2^- + H^+ = \mathbf{AgCN} + HCN.$$

Mercury (ous)

(4) Hg^+ colorless, exists in slightly or strongly acid soln.

with Cl^-: a white ppt., HgCl, insol. in acids.

with S^{--}: black ppt., Hg_2S.

Mercury (ic)

(5) Hg^{++} colorless, exists in neutral or acid soln.

with S^{--}: black ppt., HgS, insol. in acids and in HNO_3.

with Sn^{++}: reduced to Hg^+ or to Hg (ppt.).

$$2Hg^{++} + Sn^{++} = 2Hg^+ + Sn^{++++};$$
$$Hg^{++} + Sn^{++} = \mathbf{Hg} + Sn^{++++}.$$

Lead

(6) Pb^{++} colorless, exists in neutral or acid soln.

with Cl^-: a white ppt., $PbCl_2$, which, however, is somewhat sol. in hot water.

with S^{--}: black ppt., PbS, insol. in dil. acids.

with OH^-: white ppt., $Pb(OH)_2$, sol. in an excess of OH^- to form the plumbite ion:— $\mathbf{PbO_2H_2} + 2OH^- = PbO_2^{--} + 2H_2O$. PbO_2H_2, like AlO_3H_3, possesses both basic and acidic properties (see AlO_3H_3).

Bismuth

(7) Bi^{+++} colorless, exists in neutral or acid soln.

with S^{--}: black ppt., Bi_2S_3.

in dil. and very faintly acid soln. containing Cl^-: a white ppt., BiOCl, which is sol. in stronger acid:—

$$\mathbf{BiOCl} + 2H^+ \rightleftharpoons Bi^{+++} + Cl^- + H_2O.$$

Copper

(8) Cu^{++} pale blue, exists in neutral or acid soln.

with S^{--}: a dark brown ppt., CuS, insol. in dil. acid.

with OH^-: a light blue ppt., $Cu(OH)_2$, sol. in NH_4OH, forming complex ion (9).

with metallic Cu or with CN^- or I^-: it is reduced to Cu^+:— $Cu^{++} + \mathbf{Cu} = 2Cu^+$; $2Cu^{++} + 2CN^- = 2Cu^+ + (CN)_2$ (gas); $2Cu^{++} + 2I^- = 2Cu^+ + I_2$.

with $Fe(CN)_6^{----}$ in acetic acid soln.: a reddish brown ppt.

(9) $Cu(NH_3)_4^{++}$ intense, deep blue, stable in presence of slight excess of NH_4OH.

with S^{--}: brown ppt., CuS, since complex ion is somewhat dissociated into simple Cu^{++}-ions.

with CN^- in alkaline soln.: it is reduced with the formation of complex ion (10) while the blue color disappears:— $2Cu(NH_3)_4^{++} + 6CN^- = 2Cu(CN)_2^- + (CN)_2 + 8NH_3$.

(10) $Cu(CN)_2^-$ colorless, stable in alkaline soln.

with S^{--}: no ppt.

In this ion (which is analogous to $Ag(CN)_2^-$), copper is monovalent, as in the oxide Cu_2O.

Cadmium

(11) Cd^{++} colorless, exists in neutral or acid soln.

with S^{--}: a yellow ppt., CdS, insol. in dil. acids, in NH_4OH, or in KCN, but sol. in strong acids.

with OH^-: a white ppt., $Cd(OH)_2$, sol. in NH_4OH with formation of (12).

(12) $Cd(NH_3)_4{}^{++}$ colorless, exists in ammoniacal soln.; it is so much dissociated into simple ions that a ppt. is formed with S^{--}; it is not reduced by CN^- or I^-.

(13) $Cd(CN)_4{}^{--}$ colorless, exists in alkaline solns.; it is considerably dissociated into simple Cd^{++}-ions, so that a ppt. is formed with S^{--}.

Arsenic exists in different states of oxidation. Its trioxide, As_2O_3, shows weakly basic properties in that, with conc. strong acids, the As^{+++}-ion is produced. Its acidic properties are much more pronounced in that it dissolves in water to form arsenious acid, H_3AsO_3, and in bases to form salts of that acid. The pentoxide shows almost exclusively acidic properties in that it will not, on dissolving, yield positive ions, but will form only arsenic acid, H_3AsO_4, or its salts.

(14) As^{+++} colorless, exists in strongly acid soln.

with S^{--}: a yellow ppt., As_2S_3, insol. in acids, but sol. in alkalies, or alkaline sulphides: — $\mathbf{As_2S_3} + 3S^{--} = 2AsS_3{}^{---}$;

$\mathbf{As_2S_3} + 3S_x{}^{--} = 2AsS_4{}^{---} + (3x - 5)S$.

with OH^-: forms arsenious acid, AsO_3H_3, soluble, which with more OH^- gives the arsenite ion: —

$$AsO_3H_3 + 3OH^- = AsO_3{}^{---} + 3H_2O.$$

(15) $AsO_3{}^{---}$ exists in neutral or alkaline soln.

with H^+: undissociated AsO_3H_3 is formed, which, with a large excess of H^+-ions, reacts as a base with a partial formation of As^{+++}-ions: — $As(OH)_3 + 3H^+ \rightleftharpoons As^{+++} + 3H_2O$.

(16) $AsO_4{}^{---}$ exists in neutral or alkaline soln.

with Mg^{++} *and* $NH_4{}^+$ *in strongly ammoniacal soln.*: a white crystalline ppt., $MgNH_4AsO_4$.

with S^{--} in acid soln.: is reduced, very slowly in the cold, more rapidly when hot: — $AsO_4^{---} + S^{--} + 8H^+ = As^{+++} + 4H_2O + \mathbf{S}$; in a cold, strongly acid soln. a ppt. forms slowly, which is almost exclusively As_2S_5: — $2AsO_4^{---} + 5S^{--} + 16H^+ = \mathbf{As_2S_5} + 8H_2O$.

Antimony is very similar to arsenic as regards the compounds which it forms and their characteristics. It is, however, distinctly more metallic in character. Its trioxide is principally basic in its nature, although its pentoxide, like that of arsenic, is acidic.

(17) Sb^{+++} colorless, exists in acid soln.

with S^{--}: bright orange red ppt., Sb_2S_3, which is sol. in alkalies or alkaline sulphides: — $\mathbf{Sb_2S_3} + 3S^{--} = 2SbS_3^{---}$; $\mathbf{Sb_2S_3} + 3S_x^{--} = 2SbS_4^{---} + (3x - 5)S$.

with Cl^- in faintly acid soln.: a white ppt. of antimony oxychloride, SbOCl, which, however, is sol. in more conc. acid: —

$$\mathbf{SbOCl} + 2H^+ \rightleftharpoons Sb^{+++} + Cl^- + H_2O.$$

with OH^-: white ppt., $Sb(OH)_3$, insol. in excess of ammonia, and sol. only in conc. caustic alkalies.

Tin

(18) Sn^{++} colorless, exists in faintly or strongly acid soln.

with S^{--}: dark brown ppt., SnS, insol. in dil. acids, alkalies, and alkaline sulphides, but sol. in presence of S_x^{--}-ions in consequence of an oxidation: —

$$\mathbf{SnS} + S_x^{--} = SnS_3^{--} + (x - 2)S.$$

with oxidizing agents: changes with great readiness to Sn^{++++}: —

$$Sn^{++} + 2Hg^{++} = Sn^{++++} + 2Hg^+;$$
$$Sn^{++} + O + 2H^+ = Sn^{++++} + H_2O.$$

with OH^-: white ppt., $Sn(OH)_2$, sol. in an excess of strong alkali: — $\mathbf{SnO_2H_2} + 2OH^- = SnO_2^{--} + 2H_2O$.

(19) Sn^{++++} colorless, exists in acid soln.

with S^{--}: yellow ppt., SnS_2, insol. in dil. acids, but sol. in alkaline sulphides: — $\mathbf{SnS_2} + S^{--} = SnS_3^{--}$.

with OH^-: white ppt., $Sn(OH)_4$, sol. in excess of alkali: —

$$\mathbf{Sn(OH)_4} + 2OH^- = SnO_3^{--} + 3H_2O.$$

with metallic tin: it is reduced: — $Sn^{++++} + \mathbf{Sn} = 2Sn^{++}$.

with Zn: Sn^{++++} is reduced to Sn^{++}, and then, in a soln. not more than faintly acid, to metallic Sn. Sn, however, dissolves in acids: — $\mathbf{Sn} + 2H^+ = Sn^{++} + H_2$.

Iron

(20) Fe^{++} faint green, exists in neutral or acid soln.; it is easily oxidized to Fe^{+++}.

with S^{--} in alkaline soln.: black ppt., FeS, sol. in acids.

with OH^-: greenish ppt., $Fe(OH)_2$.

with $Fe(CN)_6^{----}$: white ppt., $Fe_2[Fe(CN)_6]$, which rapidly turns blue in consequence of oxidation from the oxygen of the air.

with $Fe(CN)_6^{---}$: deep blue ppt. of Turnbull's blue, $Fe_3[Fe(CN)_6]_2$.

with SCN^-: no reaction.

with CO_3^{--}: white ppt., $FeCO_3$, insol. in neutral or alkaline soln.

(21) Fe^{+++} colorless,[1] exists in faintly or strongly acid soln.

with S^{--} in acid soln.: is reduced: —

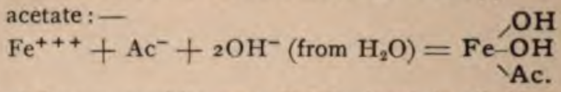
$$2Fe^{+++} + S^{--} = 2Fe^{++} + \mathbf{S}.$$

with S^{--} in alkaline soln.: black ppt., FeS, with a simultaneous production of free sulphur: —

$$2Fe^{+++} + 3S^{--} = 2\mathbf{FeS} + \mathbf{S}.$$

with OH^-: red ppt., $Fe(OH)_3$.

with Ac^- in acetic acid soln. when boiled: a red ppt. of basic ferric acetate: —



$$Fe^{+++} + Ac^- + 2OH^- \text{ (from } H_2O) = \mathbf{Fe}\begin{cases}\mathbf{OH}\\ \mathbf{OH}\\ \mathbf{Ac.}\end{cases}$$

with PO_4^{---}: a white ppt., $FePO_4$, insol. in alkalies or in acetic acid, but sol. in strong acids: —

$$\mathbf{FePO_4} + H^+ = Fe^{+++} + HPO_4^{--}.$$

with $Fe(CN)_6^{---}$: a sol. olive green complex compound.

with $Fe(CN)_6^{----}$: a blue ppt. of Prussian blue, $Fe_4[Fe(CN)_6]_3$.

with SCN^- in acid soln.: a sol. intensely blood-red, non-ionized compound, $Fe(SCN)_3$.

with solid suspended $BaCO_3$: a ppt. of $Fe(OH)_3$, which may be accounted for as follows: the ferric ion hydrolyzes easily with water, $Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$ (see Hydrolysis, pp. 42–44); but the H^+-ions produced by this reaction cannot, in the presence of suspended $BaCO_3$, attain any appreciable concentration, since they react with the latter to form CO_2 and H_2O (see Solubility of Carbonates in Acids, p. 39). Hence the hydrolysis of a ferric salt which in pure water reaches an equilibrium before any ppt. of

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[1] Neutral solutions of ferric salts are usually brown, due to the presence of small amounts of $Fe(OH)_3$ resulting from hydrolysis. The yellow color of ferric chloride solutions is due to the presence of undissociated $FeCl_3$.

$Fe(OH)_3$ is produced, can, in the presence of $BaCO_3$, continue to completion, and thus a practically complete precipitation of ferric iron can occur.

(22) $Fe(CN)_6^{----}$ a very stable ion which gives ppts. with most of the simple ions of the heavy metals.

with oxidizing agents: it is readily converted into the ferricyanide ion: — $2Fe(CN)_6^{----} + Cl_2 = 2Fe(CN)_6^{---} + 2Cl^-$.

(23) $Fe(CN)_6^{---}$ a very stable ion which, similarly to the ferrocyanide ion, forms ppts. with the simple ions of most of the heavy metals.

Aluminum

(24) Al^{+++} colorless, exists in faintly or strongly acid soln.

with OH^-: a flocculent, white ppt., $Al(OH)_3$, insol. in ammonia but sol. in strong alkalies.

AlO_3H_3 has both weakly acidic and weakly basic properties; that is, the minute quantity which dissolves in pure water dissociates in two different ways, whereby H^+- and OH^--ions, respectively, are produced: —

$$(1) \quad Al(OH)_3 \rightleftharpoons Al^{+++} + 3OH^-.$$

$$(2) \left\{ \begin{array}{l} AlO_3H_3 \rightleftharpoons 3H^+ + AlO_3^{---} \text{ or} \\ Al(OH)_3 \rightleftharpoons HAlO_2 + H_2O;\ HAlO_2 \rightleftharpoons H^+ + AlO^-_2. \end{array} \right.$$

Hence its solubility in acids and bases; for in the former case the H^+-ions of the acid destroy the OH^--ions produced by the dissociation of the aluminum hydroxide, thus allowing the dissociation (also the solution) to proceed to completion; while in the second case the OH^--ions of the base destroy the H^+-ions produced by the dissociation of the aluminic acid (H_3AlO_3 or $HAlO_2$), thus allowing the latter to continue to completion: —

$$(1) \quad \mathbf{Al(OH)}_3 + 3H^+ = Al^{+++} + 3H_2O.$$

$$(2) \left\{ \begin{array}{l} \mathbf{H_3AlO_3} + 3OH^- = AlO_3^{---} + 3H_2O \text{ or} \\ \mathbf{Al(OH)}_3 + OH^- = AlO_2^- + H_2O. \end{array} \right.$$

Ammonium hydroxide, however, does not yield OH^--ions in sufficient concentration to react with the very few H^+-ions from the H_3AlO_3, which accounts for the failure of the latter to readily dissolve in that reagent.

with Ac^- in very faintly acid soln. when boiled: a flocculent, white ppt., $Al(OH)_2Ac$.

with $BaCO_3$: ppt. of $Al(OH)_3$ (see action of $BaCO_3$ on Fe^{+++}).

Chromium

(25) Cr^{++} can exist in neutral or acid soln., but it changes with great readiness to Cr^{+++} in consequence of absorption of oxygen from the air.

(26) Cr^{+++} violet or green in color, exists in faintly or strongly acid soln.

with OH^-: a flocculent, light green ppt., $Cr(OH)_3$, insol. in ammonia and alkalies when hot, but sol. when cold in excess of alkali. CrO_3H_3, like AlO_3H_3, possesses both basic and acidic properties (see AlO_3H_3).

with Na_2O_2 and other oxidizing agents in alkaline soln.: is oxidized to the yellow chromate ion: —

$$2Cr^{+++} + 10OH^- + 3O = 2CrO_4^{--} + 5H_2O.$$

with $BaCO_3$: ppt. of $Cr(OH)_3$ (see action of $BaCO_3$ on Fe^{+++}).

(27) CrO_4^{--} in which Cr possesses the valence of VI; yellow; exists in neutral or alkaline soln.

with Ba^{++} and Pb^{++} in neutral or in acetic acid soln.: yellow ppts., $BaCrO_4$, $PbCrO_4$.

with Ag^+ in neutral soln.: red ppt., Ag_2CrO_4.

with H^+: it is converted partially or wholly into the bichromate ion: — $2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$.

(28) $Cr_2O_7^{--}$ in which, as in CrO_4^{--}, Cr possesses the valence of VI; red when concentrated; exists in neutral or acid soln.

with OH^-: changes to the chromate ion: —

$$Cr_2O_7^{--} + 2OH^- = 2CrO_4^{--} + H_2O.$$

with S^{--} and with other reducing agents in acid soln.: is reduced to the chromic ion (see p. 65): —

$$Cr_2O_7^{--} + 14H^+ + 3S^{--} = 2Cr^{+++} + 7H_2O + 3S.$$

Cobalt

(29) Co^{++} pink, exists in neutral or acid soln.

with S^{--}: a black ppt., CoS, insol. in alkalies or, after once formed, in dil. acids.

with OH^-: a light blue ppt., $Co(OH)_2$, insol. in excess of ammonia or strong alkalies, but sol. in NH_4Cl (probably due to the great decrease of the number of OH^--ions in consequence of the NH_4^+-ions from the NH_4Cl).

with CN^- in neutral soln.: a reddish brown ppt., $Co(CN)_2$, which with excess of CN^- redissolves to form the complex cobalto-cyanide ion, $Co(CN)_6^{----}$ (sol.), which by means of oxidizing agents is readily converted into the cobalti-cyanide ion, in which Co has the valence III: —

$$2Co(CN)_6^{----} + Cl_2 = 2Co(CN)_6^{---} + 2Cl^-.$$

(30) $Co(CN)_6^{---}$ an ion which can exist in both acid or basic solns. It is comparable in stability with the SO_4^{--}-ion.

with Cu^{++} in acid soln.: a very insol. light blue ppt., $Cu_3[Co(CN)_6]_2$.

Nickel

(31) Ni^{++} green, exists in acid or neutral soln.

with S^{--}: a black ppt., NiS, insol. in alkalies or, after once formed, in dil. acids.

with OH^-: a light green ppt., $Ni(OH)_2$, insol. in excess of ammonia or strong alkalies, but, like $Co(OH)_2$, sol. in NH_4Cl.

with CN^- in neutral soln.: a green ppt., $Ni(CN)_2$, which with excess of CN^- redissolves to form the complex nickelo-cyanide ion, $Ni(CN)_4^{--}$ (sol.), which is stable in alkaline or neutral soln., but with oxidizing agents yields a black ppt. of nickelic hydroxide: —

$$Ni(CN)_4^{--} + 5Cl + 3OH^- = \mathbf{Ni(OH)_3} + 2(CN)_2 + 5Cl^-.$$

Manganese

(32) Mn^{++} colorless, exists in neutral or acid soln.

with S^{--}: a flesh-colored ppt., insol. in water and in alkalies, but sol. in dil. acids and in acetic acid.

with OH^-: a white ppt., $Mn(OH)_2$, insol. in excess of alkali, but, like $Co(OH)_2$, sol. in presence of NH_4-salts.

with oxidizing agents in alkaline soln.: a black ppt. of MnO_2: —

$$Mn^{++} + Br_2 + 4OH^- = \mathbf{MnO_2} + 2H_2O + 2Br^-.$$

with PbO_2 in HNO_3 soln.: a red color of permanganate ion: —

$$2Mn^{++} + 5\mathbf{PbO_2} + 4H^+ = 2MnO_4^- + 5Pb^{++} + 2H_2O.$$

with CN^-: a brownish ppt., which with a large excess of CN^--ions redissolves to a slight extent with formation of the unstable ion, $Mn(CN)_6^{----}$.

with CO_3^{--}: a white ppt., $MnCO_3$, insol. in NH_4-salts.

with PO_4^{---} and NH_4^+ in ammoniacal soln.: a pink ppt. of $MnNH_4PO_4$.

(33) Mn^{+++} a very unstable ion.

(34) MnO_4^{--} in which Mn has a valence of VI, stable in alkaline solns., to which it imparts an intense green color.

with H^+-ions: it is unstable, and is in part oxidized to MnO_4^- at the expense of the other part, which is reduced to MnO_2: —

$$3MnO_4^{--} + 4H^+ = 2MnO_4^- + MnO_2 + 2H_2O.$$

(35) MnO_4^- in which Mn has a valence of VII, stable in neutral or acid soln.; has an intense reddish violet color.

in alkaline soln. when boiled: it changes to the green MnO_4^{--}-ion: — $2MnO_4^- + 2OH^- = 2MnO_4^{--} + H_2O + O$.

Both MnO_4^{--}- and MnO_4^--ions are strong oxidizing agents. In alkaline soln. they are reduced to MnO_2, a black ppt.; in acid soln. to Mn^{++}: —

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

Zinc

(36) Zn^{++} colorless, exists in neutral or acid soln.

with S^{--}: a white ppt., ZnS, insol. in alkalies, in neutral soln., and in acetic acid, but sol. in strong acids.

with OH^-: a white ppt., $Zn(OH)_2$, which is sol. in acids, in strong alkalies, and in ammonia. ZnO_2H_2 possesses both acidic and basic properties (see AlO_3H_3). It dissolves in strong alkalies with the formation of the negative zincate ion: — $ZnO_2H_2 + 2OH^- = 2H_2O + ZnO_2^{--}$.

Ammonium hydroxide is, however, not sufficiently dissociated into OH^- to cause the above reaction to take place; the solubility in ammonia is due rather to the formation of the complex zinc-ammonia ion: —

$$Zn(OH)_2 + 4NH_4OH = Zn(NH_3)_4^{++} + 2OH^- + 4H_2O.$$

Calcium

(37) Ca^{++} colorless, exists in neutral, acid, or weakly alkaline soln.

with OH^- when concentrated: white ppt., $Ca(OH)_2$.

with CO_3^{--}: white ppt., $CaCO_3$, which, however, is sol. in very weak acids: — $CaCO_3 + H^+ = Ca^{++} + HCO_3^-$.

with $C_2O_4^{--}$: a white ppt. of calcium oxalate, CaC_2O_4, sol. in strong acids.

with SO_4^{--}: a white ppt., $CaSO_4$, which is not entirely insol. in water.

Strontium

(38) Sr^{++} colorless, exists in neutral, acid, or alkaline soln.
with CO_3^{--}*:* a white ppt., $SrCO_3$.
with SO_4^{--}*:* a white ppt., $SrSO_4$, much less sol. than $CaSO_4$.

Barium

(39) Ba^{++} colorless, exists in neutral, acid, or alkaline solution.
with CO_3^{--}*:* white ppt., $BaCO_3$.
with CrO_4^{--} *in alkaline, neutral, or acetic acid soln.:* yellow ppt., $BaCrO_4$.
with SO_4^{--} *in neutral, acid, or alkaline soln.:* white ppt. of $BaSO_4$.

Magnesium

(40) Mg^{++} colorless, exists in neutral and acid soln.
with OH^-*:* a white ppt., $Mg(OH)_2$, which is easily sol. in NH_4-salts, probably because in the presence of NH_4^+ the OH^--ions cannot reach a sufficient concentration to give the solubility product with Mg^{++} (see $Co(OH)_2$).
with CO_3^{--} *and* $C_2O_4^{--}$*:* no ppt., if NH_4-salts are also present.
with NH_4^+ *and* PO_4^{---} *in ammoniacal soln.:* white crystalline ppt., $MgNH_4PO_4$.

Sodium, Potassium, and Ammonium

(41) Na^+, K^+, NH_4^+ colorless, exist in neutral, acid, or alkaline soln.; do not form complex ions, do not form any insol. ppts. with the common anions.
K^+ gives with $PtCl_6^{--}$ and with $Co(NO_2)_6^{---}$ characteristic difficultly sol. yellow ppts., K_2PtCl_6 and $K_3Co(NO_2)_6$, while the corresponding Na-salts are sol.
NH_4^+ gives with $PtCl_6$ likewise a difficultly sol. yellow ppt., $(NH_4)_2PtCl_6$; but it differs markedly from K^+ and Na^+ in that it forms with OH^- the very slightly dissociated body, NH_4OH, while the hydroxides of the other two metals are highly ionized.

THE IONS OF THE NON-METALS

Boron forms no simple ions. From its trioxide, B_2O_3, is derived the very weak boric acid, $B(OH)_3$, which when treated with alkalies gives salts of metaboric acid, HBO_2:— $B(OH)_3 \rightleftharpoons HBO_2 + H_2O$; $HBO_2 + OH^- \rightleftharpoons H_2O + BO_2^-$. The ion, BO_2^-, is capable of existence only in alkaline soln.

Carbon forms no simple ion.

CO_3^{--} exists in alkaline soln.

with H^+*:* first HCO_3 is formed, which with more H^+ gives the undissociated carbonic acid: — $H^+ + CO_3^{--} = HCO_3^-$; $HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$.

with the ions of most of the metals: ppts. which are sol. in dil. acids.

HCO_3^- exists only in neutral soln. It does not form ppts. with the ions of the metals unless it first breaks down to give CO_3^{--}.

$C_2H_3O_2^-$ forms no insol. salts except the slightly sol. $Ag(C_2H_3O_2)$ and certain basic acetates.

$C_2O_4^{--}$

with Ca^{++}*:* white ppt., CaC_2O_4, which is sol. in dil. acids, due to the formation of undissociated oxalic acid, $H_2C_2O_4$.

Silicon resembles boron in its tendency to form ions and in the character of the ions formed. From its dioxide, SiO_2, there is derived silicic acid, H_2SiO_3, as in a somewhat similar manner carbonic acid, H_2CO_3, is derived from CO_2. Treated with alkalies it gives the silicate ion, which is capable of existence only in alkaline soln.: — $H_2SiO_3 + 2OH^- \rightleftharpoons 2H_2O + SiO_3^{--}$

Nitrogen forms no simple ions.

NO_2^- colorless, forms no insol. compounds except the difficultly sol. $AgNO_2$. In acid soln. it forms with H^+ the weak nitrous acid, HNO_2. In such a soln. it will reduce strong oxidizing agents, whereby it is converted to the nitrate ion: —

$$2MnO_4^- + 6H^+ + 5NO_2^- = 2Mn^{++} + 5NO_3^- + 3H_2O;$$

or it will oxidize reducing agents, whereby it is converted to nitric oxide: —

$$2I^- + 4H^+ + 2NO_2^- = I_2 + 2NO + 2H_2O.$$

It is less stable than the NO_3^--ion, and is hence a more active oxidizing agent.

NO_3^- colorless, forms no insol. compounds; in acid soln. it is a strong oxidizing agent: —

$$NO_3^- + 3Fe^{++} + 4H^+ = 3Fe^{+++} + 2H_2O + NO.$$

CN^- colorless, exists in slightly alkaline and alkaline soln. It is excessively poisonous. It has a marked tendency to form complex ions with the ions of the heavy metals. It forms with H^+ the very weak hydrocyanic acid, HCN. It acts under some circumstances as a reducing agent (see action on Cu^{++}).

SCN^- colorless, exists in neutral, acid, and alkaline soln.

with Ag^+*:* white ppt., AgSCN.

with Fe^{+++}*:* an intensely red, sol., but non-ionized, compound, $Fe(SCN)_3$.

Phosphorus forms no simple ions, but with oxygen it forms several, of which the most important are those derived from phosphoric acid, H_3PO_4. This acid dissociates in three successive stages: —

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-;\ H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--};$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}.$$

In the first stage the dissociation is considerable, yielding thus a moderately strong acid; in the second it is very small; in the third it is excessively small, so that HPO_4^{--} is a very weak acid. PO_4^{---}, in neutral or alkaline soln., gives ppts. with the ions of most of the metals (see Mg^{++}), but these are sol. in dil. acids on account of the formation of undissociated HPO_4^{--} or $H_2PO_4^-$.

Sulphur

S^{--} exists in alkaline and neutral soln., but only in very small conc. in acid soln., since in presence of H^+ it forms the very weakly ionized H_2S. It gives ppts., mostly deeply colored, with the ions of the heavy metals. It acts readily as a reducing agent, whereby it is itself oxidized to free S (see Fe^{+++}).

SO_3^{--} exists in neutral and alkaline soln., and to a certain concentration in acid soln.

with Ba^{++} *and* Pb^{++}*:* white ppts. which are easily sol. in dil. acids, due to formation of undissociated H_2SO_3.

with oxidizing agents: it is converted to SO_4^{--}: —

$$SO_3^{--} + O = SO_4^{--}.$$

SO_4^{--} exists in acid, neutral, and alkaline soln.

with Pb^{++} *and with* Ba^{++}*:* white ppts., $PbSO_4$, $BaSO_4$, insol. in acids and alkalies.

$S_2O_3^{--}$ exists in neutral and alkaline soln.

with H^+*:* it is decomposed: —

$$S_2O_3^{--} + 2H^+ \longrightarrow H_2S_2O_3 \longrightarrow H_2O + SO_2 + S.$$

Fluorine

F^- *with* Ca^{++}, Ba^{++}, Pb^{++}: ppts. of CaF_2, BaF_2, PbF_2, which, however, are sol. in dil. strong acids on account of the formation of undissociated HF.

Chlorine

Cl^- forms but few insol. comps. (see Ag^+, Hg^+, and Pb^{++}).

with strong oxidizing agents: it is changed to free chlorine, *e.g.*:—

$$2Cl^- + MnO_2 + 4H^+ = Mn^{++} + 2H_2O + Cl_2.$$

with oxidizing agents in alkaline soln.: it is converted to the hypochlorite ion, ClO^-, and to the chlorate ion, ClO_3^-:—

$$Cl^- + Cl_2 + 2OH^- = ClO^- + 2Cl^- + H_2O;$$

$$Cl^- + 3Cl_2 + 6OH^- = ClO_3^- + 6Cl^- + 3H_2O.$$

ClO_3^- forms no insol. comp.

with reducing agents: it is changed to the simple ion:—

$$ClO_3^- + 3SO_3^{--} = 3SO_4^{--} + Cl^-.$$

Bromine forms ions analogous to those of chlorine.

Iodine forms ions analogous to those of chlorine and bromine; it is a strong reducing agent, *e.g.*:— $2I^- + 2Cu^{++} = 2Cu^+ + I_2$.

CHAPTER VI

EXPERIMENTS ILLUSTRATIVE OF THE THEORY OF ELECTROLYTIC DISSOCIATION, AND SOME OF ITS APPLICATIONS

THE following series of experiments is designed to accompany the study of the preceding text. The important points to be learned from each experiment are indicated by the italicized questions to be answered by the student. The actual performance of the experiments will be found to be comparatively simple, but satisfactory laboratory notes should contain much more than the mere records of observations, and such notes can only be written after careful, thoughtful study of the related portions of the foregoing chapters. The student should also consult frequently with his instructors, and explanations and corrections on the part of the latter must be painstaking and complete if the laboratory experimentation is to serve its purpose.

Apparatus. — The only special apparatus required for these experiments is that for the testing of electrical conductivity.[1]

Figure 5 is a diagram of the entire apparatus as mounted on a standard. The terminal wires, as represented by the symbols + and − may be extended by means of a lamp cord and plug, the latter of which may be screwed into a lamp socket of a 110-volt, incandescent lighting system. Either direct or alternating current may be used, although the former is somewhat to be preferred.

The terminal wires, as represented, extend along the length of the standard. One of them is connected with one binding screw of each of three incandescent lamp sockets; the other wire is attached to one binding post of each of three pairs. The other binding post of each pair is connected with the other binding screw of the lamp socket above it. From the pairs of binding posts are suspended three different forms of electrodes, designated *A*, *B*, and *C*. The apparatus is thus so

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[1] This form of apparatus was designed in the laboratories of the Massachusetts Institute of Technology, where it has been in successful use for two years.

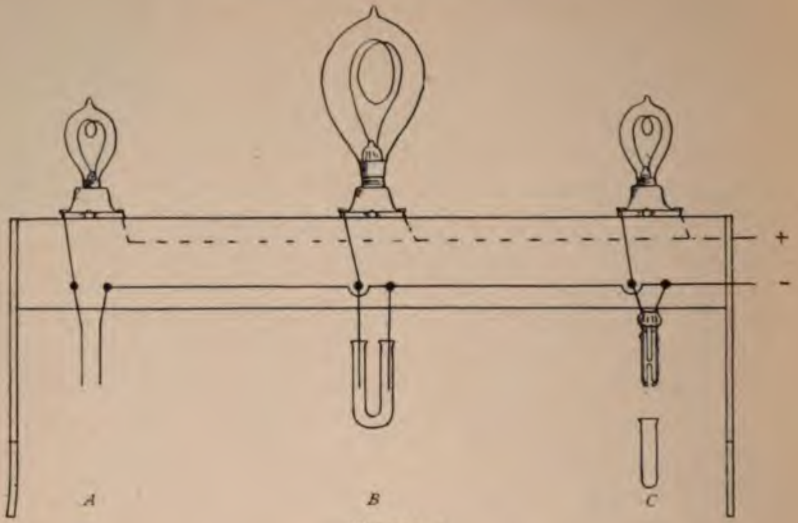

FIGURE 5

arranged that if a substance of unknown conductivity is introduced between two electrodes belonging to one of the pairs, an electric current will pass in proportion to the conductivity of the substance. Since this current must also pass through the lamp directly above, this will glow with a brilliancy roughly proportional to the amount of current.

Electrodes *A* consist of stout copper wires, and are to be used in testing the conductivity of solid substances, lumps of which are held with the fingers in such a way as to come into contact with each electrode. A 16-candle power lamp may be used in the socket above.

Electrodes *B* consist of similar copper wires, but bent far enough apart so that they will pass into the two arms of a U-tube 8 mm. internal diameter and 7 cm. high, when the latter is raised from underneath. A 50-candle power lamp (or, somewhat less satisfactorily, a 32-candle power lamp) should be used with these electrodes, which are then designed to show differences in conductivity among good conductors.

Electrodes *C* consist of fine platinum wires supported upon glass rods [1], as shown in Figure 6, and are to be used with a 16-candle power

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[1] A pattern of Electrode *C* has been furnished to the L. E. Knott Apparatus Company, Boston, who are in a position to furnish this part of the apparatus. The remainder of the apparatus may be constructed by any carpenter.

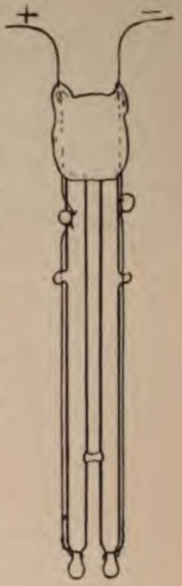

FIGURE 6

lamp. They are to be used in testing the conductivity of liquids, the latter to be placed in 3-inch test tubes, which may be raised until the electrodes are immersed in the liquid. Electrodes *A* could be used in the same way, but have the disadvantage that they are strongly attacked by the liquid during the passage of the current.

1. **The Electrical Conductivity of Different Types of Substances.** — Test the conductivity of water, alcohol, and pure acetic acid.

Select any two solid salts in the laboratory. Test the conductivity of each by holding a small lump so as to touch both electrodes. Dissolve not more than 0.25 gram of each in a 3-inch test tube of pure water, and test the conductivity of the solution.

Test the conductivity of diluted solutions of sodium hydroxide and of hydrochloric acid. Dilute about 0.5 c.c. of pure acetic acid with water in a small test tube, and test its conductivity.

Dissolve a little sugar in water; also mix about 1 c.c. of alcohol with 5 c.c. of water. Test the conductivity of each solution.

Classify the substances used above according to their electrical conductivities.

2. **Properties of Acids.** — Compare the conductivity of dilute hydrochloric acid, dilute sulphuric acid, dilute acetic acid, and pure water. Compare the taste of each of the acids by stirring a few drops into a small beaker of water and tasting one drop of the resulting solution. Compare the action of each on a piece of zinc, touching the zinc with a platinum wire if the acid alone has no effect. Compare the effect of each upon litmus paper.

Name four components of an acid solution. What is the relative amount of these components in the different acid solutions examined? What component is common to all acids, and how does the strength of an acid depend on the amount of this component?

3. **Properties of Bases.** — Dissolve about 1 gram of sodium hydroxide in 10 c.c. of water. Dilute about 2 c.c. of concentrated ammonium hydroxide solution (sp. gr. 0.90) with 10 c.c. of water.

Compare these two solutions with respect to (*a*) conductivity, (*b*) effect upon litmus, (*c*) taste (after diluting very considerably), (*d*) slippery feeling upon rubbing a drop of the solution between the fingers.

Name four components of each solution. What is the relative amount of each component? What component is common to the solutions of all bases, and how does the strength of a base depend upon the amount of this component?

4. **Neutralization of an Acid and a Base.** — Run 10 c.c. of a normal solution of HCl from a burette into a dry beaker. Add one drop of a litmus solution, and then run in slowly from another burette a normal solution of NaOH, until a single drop just changes the color to blue. Make sure that one drop of HCl will now cause the red color to reappear.

Arrange such a form of conductivity vessel that the distance between the electrodes can be so adjusted that, with a normal solution of hydrochloric acid, the filament of the lamp will glow faintly. The apparatus described with Electrodes *B* serves well for this purpose.

With this apparatus compare the conductivity of both the acid and the base separately with that of the neutralized solution.

What component of each solution has disappeared during the neutralization? What components have not been affected by the process? Write the equation for this reaction. What is the cause of the completeness of this reaction?

5. **The Law of Mass Action.** — Place 2 c.c. of a saturated solution of silver acetate in each of two test tubes. Add to one tube a small crystal of silver nitrate (not more than 0.05 gram). Agitate the solution until the crystal has completely dissolved. If no change is noticed at once, set the tube aside for several minutes and observe again.

To the second tube add a small crystal of sodium acetate instead of silver nitrate, and observe as before.

Note 1. Silver acetate is only slightly soluble, that is, about 10 grams per liter at 20° C.

Note 2. Put all the waste from this experiment in the bottle marked silver residues.

Repeat the above experiment, substituting a saturated solution of potassium chlorate for that of silver acetate. Dissolve in two portions of this, respectively, small crystals of potassium chloride and sodium chlorate, and observe as above.

Explain the application of the Mass Action Law in these experiments. Define what is meant by solubility product.

6. **Neutralization of a Weak Acid and a Weak Base.** — Neutralize 10 c.c. of a normal solution of acetic acid with a normal solution of ammonium hydroxide. (See Experiment 4.)

Compare the conductivity of the acid and the base separately with that of the neutralized solution. Use Electrodes *C.*

Compare the ionization of weak bases and acids with that of their salts, and explain how during the process of neutralization the concentrations of the various components change in accordance with the Principle of Mass Action.

7. **The Displacement of a Weak Acid from Its Neutral Salt by a Stronger Acid.** — (*a*) To 2 c.c. of sodium benzoate solution (50 grams per liter) add a few drops of hydrochloric acid, (sp. gr. 1.12). Sodium benzoate is a strong electrolyte, yielding Na^+- and $(C_7H_5O_2)^-$-ions.

Eliminating all the possible components which may have been formed with the properties of which we are already acquainted, what must be the new substance the formation of which is made evident?

(*b*) Heat 2 c.c. of sodium acetate solution. Do you observe any odor to the solution? Add 2 c.c. of dilute sulphuric acid, (sp. gr. 1.25) and heat again. What odor do you now observe?

Explain, in accordance with the Principle of Mass Action, the formation of the component which is detected by this odor.

(*c*) To 5 c.c. of sodium carbonate solution add acetic acid, a few drops at a time, till action ceases. What is the gas formed?

If this gas were prevented from escaping, by keeping the solution under a heavy pressure, what component would then form which otherwise would not form to any considerable extent? Write the equations showing the conditions of equilibrium between the different components of this solution. How does the escape of the gas affect these conditions?

(*d*) Treat a small quantity of marble dust (calcium carbonate) with some dilute hydrochloric acid, and see if it will all dissolve.

Is calcium carbonate appreciably soluble in water? Can you explain *the solvent action of hydrochloric acid in the same manner as you explained the action of the acid in (c)? If so, what must be true concerning the solubility of calcium carbonate in pure water?*

8. **The Displacement of a Weak Base from Its Neutral Salt by Means of a Stronger Base.** — (*a*) Warm 2 c.c. of ammonium chloride solution, and observe if there is an odor. Add 2 c.c. of sodium hydroxide solution, and again observe if there is an odor.

What new component is here shown by the odor to have been formed? To how great an extent was it formed? Explain what further change a small fraction of this component undergoes to produce the substance which gives the odor.

(*b*) To 2 c.c. of magnesium sulphate solution add a little sodium hydroxide solution.

What is the new substance which is formed? Had this new substance not been insoluble, to how great an extent would it have formed?

9. **Tests for the Presence of Certain Ions in a Solution.** — (*a*) Place some concentrated calcium chloride solution in one test tube, and dilute one drop of it in another with one-half of the test tube full of water. Add a drop or two of dilute sulphuric acid to each.

What is the precipitate formed in one case? Could its formation be used as a test for one of the ions of calcium chloride? If so, would it be a delicate test? What may be said of the solubility product of the precipitate?

Test the electrical conductivity of a saturated solution of this substance.

(*b*) Pour 4 c.c. of silver nitrate solution into a test tube, and dilute with water enough to half fill the tube. Then add a solution of sodium chloride until precipitation is complete. Pour the contents of the tube through a filter, and wash the filter with pure water until 1 c.c. of the wash water gives no turbidity with a drop of silver nitrate. Now break the point of the filter with a glass rod, and wash the precipitate into a 3-inch test tube together with 4 c.c. of water. With the thumb over the mouth of the tube, shake thoroughly for some moments; then, without filtering, test the electrical conductivity of the liquid.

To one test tube half full of water add one drop of silver nitrate; to another add one drop of sodium chloride solution. Pour the contents of the two tubes together.

What is the new substance formed in this experiment? For what ion is its formation a test? Is this a delicate test? How does the solubility product of this substance compare with that of calcium sulphate? What components were contained in the liquid which ran through the filter, and in what relative amounts? If this liquid had been evaporated, what would have been the nature of the residue? Which components disappeared during the evaporation, and which increased in amount?

(*c*) Add a drop of silver nitrate solution to 3 c.c. of each of the following solutions: calcium chloride, cobalt chloride, copper chloride. Add a drop of silver sulphate solution to some sodium chloride solution.

What ion is common to all aqueous solutions of metallic chlorides? Of simple silver salts?

(*d*) Mix 1 c.c. of alcohol with 3 c.c. of water. Add three drops of chloroform, and mix by shaking. Test the conductivity of this solution, and then add a drop of silver nitrate solution.

Account for the different behavior of chlorine in this compound and in such compounds as sodium chloride.

10. **Simple and Complex Ions.** — (*a*) Add a few drops of lead nitrate solution to 3 c.c. of solutions of (1) sodium sulphide, (2) sodium sulphate, (3) sodium thiosulphate.

Account for the different behavior of sulphur in these three compounds.

(*b*) Add a drop of silver nitrate to solutions of potassium chlorate and chloracetic acid, ($HC_2H_2ClO_2$).

(*c*) Add 5 c.c. of ammonium hydroxide (sp. gr. 0.96) to 1 c.c. of dilute silver nitrate solution, and then add some potassium chloride solution.

What has become of the silver ions?

11. **The Power of Solvents Other than Water to Cause Electrolytic Dissociation.** — (*a*) Test a solution of hydrogen chloride in toluene with regard to (1) its conductivity; (2) its action upon a bit of marble; (3) its action upon a piece of zinc. Touch the zinc beneath the liquid with a platinum wire. All apparatus and materials used in this experiment must be perfectly free from moisture.

What are the components of this solution? How does a solution of hydrogen chloride in toluene differ from one in water?

(*b*) To 2 c.c. of the above solution in a small test tube add 2 c.c. of water, and shake. Now insert the electrodes till they dip in the aqueous layer.

(*c*) Test a solution of hydrogen chloride in absolute alcohol as in (*a*).

12. **The Relative Electrolytic Solution Tension of Different Metals.** — (*a*) Place some scraps of zinc in 5 c.c. of dilute copper sulphate solution. Allow them to stand, with frequent shaking (why?), until the chemical change is complete. Pour off a little of the clear liquid and add a little ammonia water to it. Add also ammonia water to some copper sulphate solution. Add some ammonium sulphide to another small portion of the liquid, and also to some zinc sulphate solution.

What ions are shown to be present or absent by the tests with ammonia water and with ammonium sulphide? What has caused the above change?

(*b*) Put some pieces of copper wire in 2 c.c. of silver nitrate solution. After standing a few minutes test the liquid for silver ions.

What can be said of the relative electrolytic solution tension of the metals studied in (*a*) *and* (*b*)*? Judging from the behavior of these metals with acids, where would you place hydrogen in this classification?*

13. **The Relative Tendency of Non-metallic Elements to Pass into the Ionic Form.** — (*a*) Add bromine water and iodine solution to separate portions of hydrogen sulphide water.

(*b*) What is the effect of a solution of each of the free halogens upon solutions of the potassium or hydrogen compounds of the other halogens? (If you do not know this, try the necessary experiments with solutions to be found in the laboratory.) To test for the presence of free bromine or iodine in a solution add about 1 c.c. of carbon bisulphide to the liquid; shake, and allow the globule of carbon bisulphide to settle. This will have collected the free halogen, imparting to it, if bromine, a red color; if iodine, a violet color.

(*c*) What substance separates from a solution of hydrogen sulphide which has been allowed to stand where it could absorb oxygen, as in a bottle the stopper of which is frequently removed?

Arrange the halogens, sulphur, and oxygen, as nearly as you can tell from the data in (*a*), (*b*), (*c*), *in the order of their tendency to take the form of negative ions.*

14. Hydrolysis. — (*a*) Dissolve about half a gram each of zinc sulphate, sodium chloride, and sodium carbonate in a little water, and test each solution with red and blue litmus.

Explain the relation of hydrolysis to the observed results.

(*b*) Place 1 c.c. of a concentrated solution of zinc chloride in a test tube. Fill the tube half full with water. Now add hydrochloric acid drop by drop till the precipitate disappears.

Assuming the precipitate to have been basic zinc chloride, $\mathrm{Zn}{<}^{\mathrm{OH}}_{\mathrm{Cl}}$, *explain its formation from the components of the solution, and explain why a slight excess of hydrochloric acid causes its disappearance.*

* * *

15. Saturate 5 c.c. of a 10-per cent. zinc chloride solution with hydrogen sulphide. Filter off the precipitate, and add to the filtrate some ammonium sulphide.

To a second portion of zinc chloride solution add 1 c.c. of dilute hydrochloric acid (sp. gr. 1.12), and again saturate with hydrogen sulphide.

To a third portion of zinc chloride solution add 2 c.c. of concentrated sodium acetate solution, saturate with hydrogen sulphide, filter, and to the filtrate add ammonium sulphide.

Explain how the degree to which hydrogen sulphide can dissociate is affected by the components present in the three cases above, and what effect the degree of this dissociation has upon the formation of a precipitate.

16. Prepare four samples of sulphuric acid of different strengths, as follows: —

1. Dilute 1 volume of acid of 1.25 sp. gr. with an equal volume of water.
2. To 2 volumes of acid of 1.25 sp. gr. add 1 volume of concentrated acid, sp. gr. 1.84.
3. To 1 volume of water add 4 volumes of acid, sp. gr. 1.84.
4. To 3 volumes of acid, 1.84 sp. gr., add 1 volume of fuming sulphuric acid. This yields a liquid which contains a slight excess of SO_3.

Test the conductivity of each of these liquids, using Electrodes *B*.

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Treat each with feathered zinc, warming after observing whether any action takes place in the cold. Test the gases evolved in each case for hydrogen, sulphur dioxide, and hydrogen sulphide, and observe also if any sulphur collects on the sides of the tube.

Repeat the above experiments, using copper turnings instead of feathered zinc.

Draw conclusions from the conductivity and from the products formed in each case as to what must have been the components of the liquid, and explain how the relative electrolytic solution tensions of zinc, hydrogen, and copper affect the result.

APPENDIX

DEGREE OF DISSOCIATION OF SOME OF THE MOST IMPORTANT ELECTROLYTES

SALTS

NEUTRAL salts, with very few exceptions, are highly dissociated. If they are classified, as in the table below, according to the valence of their ions, it is found that all belonging to any one class have practically the same degree of dissociation. The four classes which are indicated may be typified by KNO_3, $Ba(NO_3)_2$, K_2SO_4, and $ZnSO_4$, respectively.

Type of salt.	Percentage dissociation in 0.1 equivalent solution.
R^+R^-	86
$R^{++}R_2^-$	72
$R_2^+R^{--}$	72
$R^{++}R^{--}$	45

ACIDS

Substance.	Percentage dissociation in 0.1 equivalent solution.
HCl, HBr, HI, HNO_3 $HClO_3$, $HClO_4$, $HMnO_4$	90
H_2SO_4	60
$H_2C_2O_4$	34
H_2SO_3	20
H_3PO_4	13
H_3AsO_4	11
HF	9
$HC_2H_3O_2$	1.4
H_2CO_3	0.12
H_2S	0.05
HCN	0.01

BASES

Substance.	Percentage dissociation in 0.1 equivalent solution.
KOH, NaOH	86
$Ba(OH)_2$	75
NH_4OH	1.4

$Ca(OH)_2$, $Mg(OH)_2$ are but slightly soluble, but so far as they do dissolve they are dissociated to about the same extent as $Ba(OH)_2$ in a solution of the same concentration.

The hydroxides of the heavy metals are very insoluble and, as a rule, very weakly basic.

AgOH is soluble to the extent of one part in 15,000 of water, in which solution about 33 per cent. of its molecules are ionized. It is thus a moderately strong base.

Hydroxides of the type $Zn(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$ are much less basic than AgOH, while hydroxides of the type $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ are least basic of all.

The dissociation of pure water into H^+- and OH^--ions amounts to only $\frac{2}{10000000}$ of 1 per cent.

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